

NOBIS 96.024
HYDROGEN AS INDICATOR FOR IN SITU REDOX
CONDITION AND DECHLORINATION

Phase 1

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Samenvatting

Intrinsieke biodegradatie en gestimuleerde natuurlijke afbraak van chloorkoolwaterstoffen (zoals PER en TRI) zijn belangrijk bij in situ reiniging van grondwater vervuild met deze stoffen. Het doel van dit project was de bruikbaarheid van waterstofmetingen als aanvullende redoxkarakteristiek en als graadmeter voor de in situ dechloreringsconditie in de praktijk te toetsen. Op drie met chlooroplosmiddel verontreinigde locaties en in het grondwater nabij een stortplaats zijn waterstofmetingen in combinatie met andere bepalingen uitgevoerd. Verschillende methoden om deze gegevens te interpreteren zijn gebruikt en met elkaar vergeleken.

Uit het onderzoek is naar voren gekomen dat redoxkarakterisering door middel van het meten van waterstof wordt gekenmerkt door een goede prijs/prestatie-verhouding. Met waterstofmetingen kan een eerste snelle on-site screening van de redoxsituatie worden verricht. Vervolgens kan een voldoende gedetailleerde redoxkarakterisering worden verkregen door gericht een aantal punten te kiezen en naast waterstof ook de macrochemische parameters te bepalen. Het weglaten van waterstofmetingen lijkt in een aantal gevallen een onvolledig en niet consistent beeld op te leveren.

Het meten van waterstof in grondwater is waarschijnlijk ook bruikbaar voor het inschatten van de in situ dechloreringsconditie. Bij in situ waterstofconcentraties hoger dan 2 nM is een hoge mate van dechlorering gevonden. In aanwezigheid van voldoende DOC, BTEX, minerale olie, en 1,2-dichloorethaan blijkt de waterstofconcentratie verhoogd te zijn en ook een hoge mate van dechlorering op te treden. Enkele kennisleemten moeten nog worden aangepakt om de toepassing van een waterstofmeting als indicator voor dechlorering volwaardig te maken.

Trefwoorden**Gecontroleerde termen:**

dechlorination, field research, hydrogen, redox condition

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Abstract

The use of intrinsic degradation processes (natural attenuation) is becoming the basis for the restoration of contaminated sites. Within this context, measuring concentrations of hydrogen in groundwater is important in two ways. Firstly, the hydrogen concentration can be used to characterise in situ redox conditions. Secondly, hydrogen may be an indicator for the in situ condition for dechlorination. These two potential applications of hydrogen measurements were tested by field research at three sites contaminated with chlorinated solvents and at one landfill site. Besides hydrogen concentrations, other groundwater chemical parameters were also determined. Different methods for data interpretation were used and compared.

Redox characterisation using hydrogen measurements proved to be a cost-efficient method to characterise the redox situation at chlorinated solvent sites. A quick on-site scan of the redox situation can be performed using hydrogen measurements. Subsequently, an adequate and detailed redox profile can be determined by selecting sampling points where hydrogen is measured and groundwater samples are taken for analyses on other chemical parameters. At some of the sites it was shown that omitting the hydrogen data results in an inconsistent redox identification.

Hydrogen may indeed be an indicator for the in situ dechlorination condition. At hydrogen concentrations higher than 2 nM, a high degree of in situ dechlorination was observed. In wells where relatively high amounts of DOC, BTEX, mineral oil, or 1,2-dichloroethane were detected, elevated hydrogen concentrations together with higher degrees of dechlorination were observed. Several knowledge gaps still need to be resolved to bring this application of hydrogen measurements to a mature state.

Keywords

Controlled terms:

dechlorination, field research, hydrogen,
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PREFACE

With this report, the first phase in the NOBIS project 'Hydrogen as indicator for in situ redox condition and dechlorination' (project number 96.024), has been delivered. The aim of this project is twofold and divided into two phases. In the first phase a method was developed to demonstrate the usefulness of hydrogen measurements as an extra redox identification method and as an indicator for in situ dechlorination. This method was tested at four locations.

In the second phase a multiple location analysis is planned in order to determine the correlation of hydrogen and other parameters by specific measurements at the locations, followed by a principal component analysis of relations between hydrogen concentrations and these parameters.

The first phase of this project was carried out by TNO Institute of Environmental Sciences, Energy Research and Process Innovation, Department of Environmental Biotechnology. During the measurements at the different sites TNO was assisted by various persons and organisations listed below.

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DAF, Eindhoven	Grontmij, Houten	Paul Verhaagen
SBNS, Tilburg	IWACO, Den Bosch	Simon Hofstra
Banisveld, Boxtel	IWACO, Rotterdam	Timo Heimovaara
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SAMENVATTING

Hydrogen as indicator for in situ redox condition and dechlorination

Intrinsieke biodegradatie en gestimuleerde natuurlijke afbraak van chloorkoolwaterstoffen (zoals PER en TRI) zijn belangrijk bij de beheersing en extensieve reiniging van grondwater die vervuild zijn met deze stoffen. De sanering van bodems die verontreinigd zijn met PER en TRI zijn in de meeste gevallen complex en kostbaar. Een mogelijkheid om de kosten van deze saneringen te beperken, en daarmee de (financiële) haalbaarheid te vergroten, is het bewust gebruik maken en stimuleren van natuurlijke processen. Hiertoe is het belangrijk dat de bodem de juiste intrinsieke dechloringsconditie heeft. Dat wil zeggen dat de juiste redoxpotentiaal voor reductieve dechlorering moet heersen, de aanwezigheid van voldoende elektronendonor en -acceptor en de geschikte microbiële populatie aanwezig moet zijn.

De op locatie gemeten concentratie van waterstof in grondwater kan mogelijk als een graadmeter worden gebruikt om de intrinsieke dechloringsconditie van een watervoerend pakket vast te stellen. Daarnaast kan met waterstofmetingen een meer completere redoxkarakterisering worden uitgevoerd, hetgeen belangrijk is voor een effectief gebruik van natuurlijke of gestimuleerde biologische afbraak.

Het onderzoek is opgedeeld in twee fasen. De eerste fase bestaat uit het opzetten van een meetmethode en het testen van deze methode, het meten van waterstof op vier verschillende locaties en het interpreteren van deze gegevens. De tweede fase, die nog niet is uitgevoerd, bestaat uit een multilocatie-analyse waarbij wordt getracht correlaties tussen waterstof en andere parameters (o.a. DOC, macrochemie) te identificeren.

In dit rapport wordt de eerste fase besproken. Deze fase heeft gelopen van mei 1998 tot en met maart 1999.

Doel

Dit onderzoek had tot doel de bruikbaarheid van waterstofmetingen te onderzoeken. Enerzijds om de intrinsieke dechloreringsconditie van een watervoerend pakket vast te stellen en anderzijds om na te gaan of de waterstofconcentratie kan worden gebruikt als een goede redoxkarakteristiek.

Werkzaamheden tijdens fase 1

In de eerste fase van dit onderzoek zijn de volgende onderdelen uitgevoerd:

1. Uitwerken en verhelderen van de grondslagen voor de interpretatie van waterstofmetingen ten behoeve van de karakterisering van de redoxsituatie en van het natuurlijke afbraak potentieel.
2. Testen van apparatuur en opstellen van een methode voor on-site bemonstering en analyse van waterstof.
3. Uitvoering van waterstofmetingen op een aantal locaties en interpretatie op basis van geformuleerde grondslagen (1) voor het gebruik van waterstof als indicator voor redoxkarakterisatie en voor natuurlijke biodegradatie van chloorkoolwaterstoffen. Gaande het project zijn uiteindelijk vier locaties in het meetprogramma opgenomen, te weten:
 - drie locaties, die verontreinigd zijn met chloorkoolwaterstoffen en in mindere mate met BTEX, namelijk:
 - de locatie Rademarkt te Groningen;
 - het DAF-terrein te Eindhoven;
 - het NS-revisieterrein te Tilburg.

- één stortplaats, die verontreinigd is met zware metalen, aromaten en chloorkoolwaterstoffen, namelijk:
 - Banisveld te Boxtel.

De resultaten van de waterstofmetingen zijn per locatie vergeleken met andere redoxparameters en met de dechloreringsindex. Vervolgens zijn de resultaten voor de vier verschillende locaties met elkaar vergeleken en is een inschatting gemaakt van de toegevoegde waarde van de waterstofmetingen voor redoxkarakterisering en het inschatten van de mate van dechlorering. Een samenvatting van de bevindingen is hieronder weergegeven.

Uitwerken en verhelderen van de grondslagen

In de theoretische hoofdstukken 2 en 3 is geanalyseerd en beschreven wat de rol van waterstof is bij de in de bodem optredende redoxprocessen die grotendeels door micro-organismen worden gekatalyseerd. Waterstof is een tussenproduct dat gevormd wordt bij de natuurlijke microbiologische fermentatie en vertering van organisch materiaal in de bodem. Het gevormde waterstof reageert met behulp van micro-organismen en vervolgens met andere in de bodem aanwezige componenten. Het waterstof is een elektronendonor en geeft daarbij elektronen af aan die componenten. Dit kunnen natuurlijke elektronenacceptoren zijn zoals zuurstof, nitraat, ijzer(III), sulfaat, en kooldioxide, maar ook verontreinigingen zoals PER, TRI en andere chloorkoolwaterstoffen, die daarbij gedechloriseerd worden (zie fig. 1)

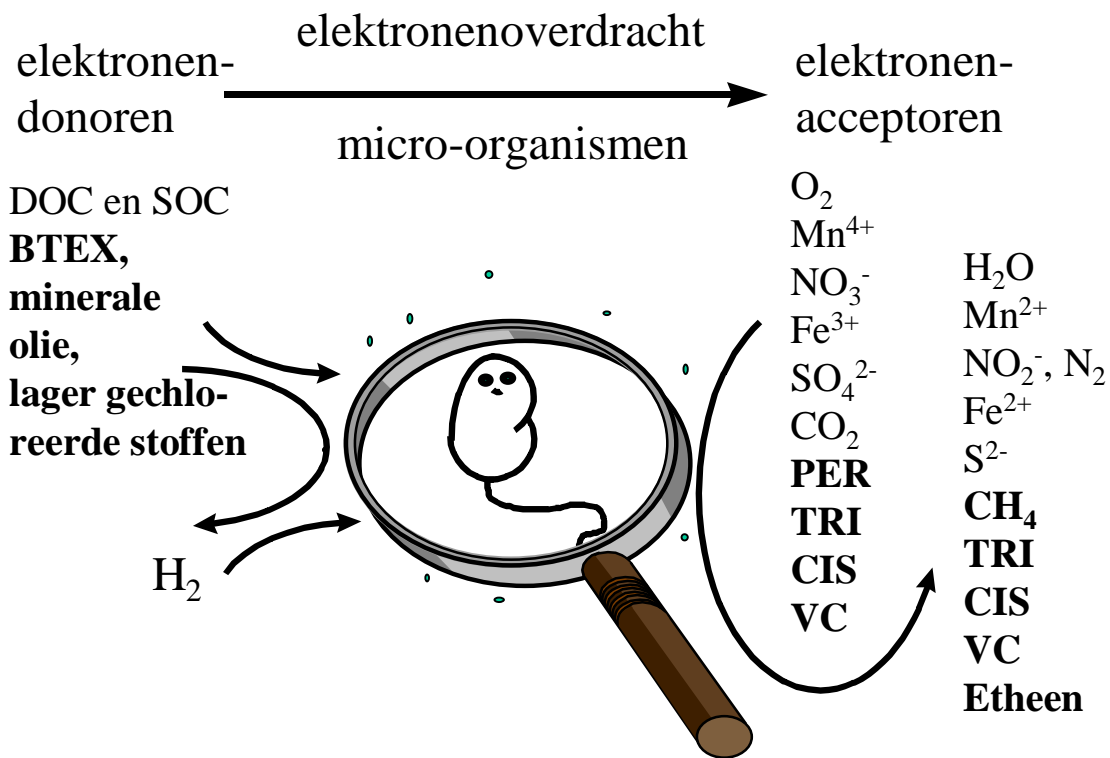


Fig. 1. Rol van waterstof en micro-organismen bij de in de bodem optredende processen.

Het concentratieniveau van waterstof in het grondwater wordt aldus bepaald door een complex geheel van processen waarbij enerzijds waterstof wordt geproduceerd uit organische stof en anderzijds waterstof wordt geconsumeerd door de reactie met bodem- en grondwaterbestanddelen. In deze studie is geïnventariseerd welke mechanismen, en welke biologische en chemische parameters relevant kunnen zijn. Voor een gedetailleerde beschrijving wordt verwezen

naar de betreffende hoofdstukken in dit rapport. Hier wordt volstaan met het geven van enkele hoofdpunten.

In een niet te zeer verstoord bodemsysteem zijn de processen vaak in (dicht bij) evenwicht en correspondeert de waterstofconcentratie met het heersende redoxmilieu. Een aantal onderzoekers hebben *ranges* van waterstofconcentraties proefondervindelijk (empirisch) gerelateerd aan de heersende (dominante) redoxconditie. Deze empirische benadering kan aldus worden gebruikt voor de interpretatie van gemeten waterstofconcentraties ten behoeve van de redoxkarakterisatie (zie fig. II).

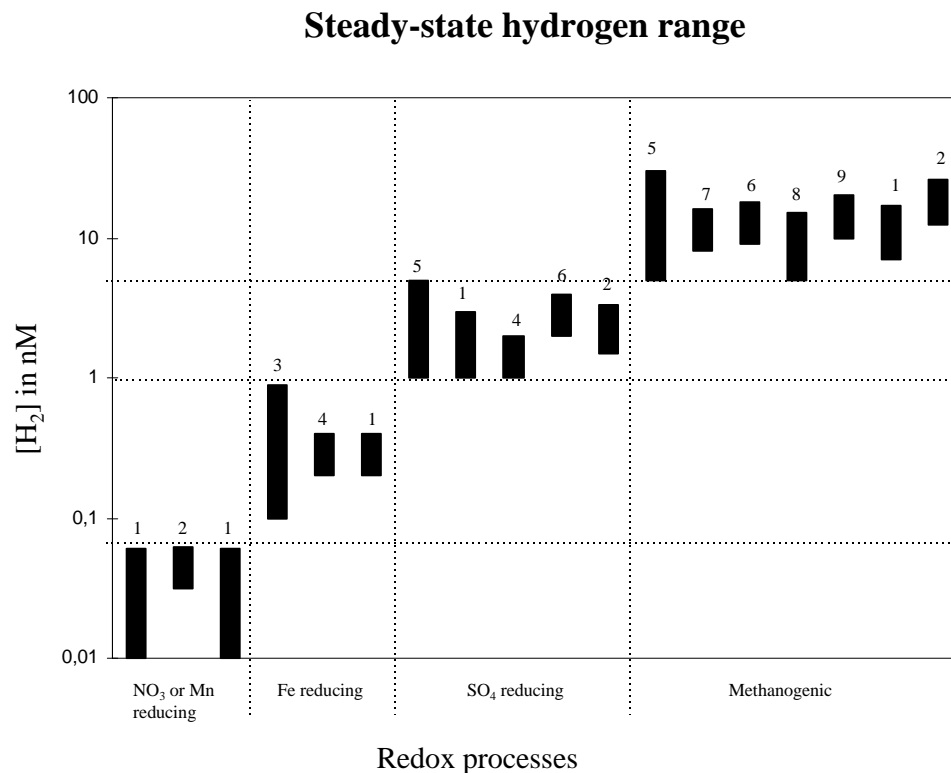


Fig. II. Overzicht van steady-state H₂-concentraties gerelateerd aan verschillende redoxprocessen bij standaardtemperatuur (25 °C). De waarden zijn afkomstig uit de volgende referenties: 1: [Lovley and Goodwin, 1988]; 2: [Hoehler et al., 1998]; 3: [Chapelle and Lovley, 1992]; 4: [Lovley and Philips, 1987]; 5: [Vroblesky and Chapelle, 1994]; 6: [Lovley et al., 1982]; 7: [Lovley and Klung, 1982]; 8: [Goodwin et al., 1988]; 9: [Conrad et al., 1987].

Deze **empirische relatie** kan dus worden gebruikt voor de redoxkarakterisering aan de hand van waterstofmetingen. Belangrijk daarbij is dat rekening wordt gehouden met de lokaal heersende temperatuur van de bodem. In dit rapport zijn correctiefactoren voor de temperatuur opgenomen.

De meetwaarden van waterstof kunnen ook worden geïnterpreteerd door combinatie met macrochemische gegevens van de bodem en het grondwater en vervolgens de uitvoering van **thermodynamische berekeningen** (in dit rapport ook wel de partiële evenwichtsbenadering genoemd). Op deze manier kan voor een bepaald monsterpunt worden aangetoond welke redoxprocessen *kunnen* verlopen. Dit kan voor 'normale' redoxprocessen, maar ook voor dechloreringsreacties.

Het voordeel van de thermodynamische methode is dat deze locatie onafhankelijk is; er zijn geen locatiespecifieke criteria waarmee wordt vastgesteld welke redoxprocessen kunnen optreden. Uit

de inventarisatie kwam nog wel een belangrijke kennisleemte naar voren. De minimale energie die micro-organismen uit een redox- en dechloreringsreactie moeten kunnen winnen om daarop te kunnen leven is een invoerparameter in de thermodynamische evaluatie. Er konden slechts zeer algemene waarden voor deze minimale energieën in de literatuur worden gevonden. In dit onderzoek is bij alle thermodynamische berekeningen standaard een waarde voor de minimale energiebehoefte van 5 kJ/mol gebruikt. Zeker voor de dechloreringsreacties is het mogelijk dat de werkelijke waarden veel hoger liggen. Voor dechloreringsreacties, waarbij waterstof een rol speelt, heeft een grote minimale energiebehoefte het effect dat er een relatief hoge grensconcentratie voor waterstof bestaat. De waterstofconcentratie moet dan deze waarde overstijgen om dechlorering te kunnen laten plaatsvinden.

Voor een bodemsysteem dat ver uit evenwicht is, is de situatie veel complexer. Dit kan voorkomen bij stortplaatsen waar recentelijk grote hoeveelheden vers organische stof in de bodem zijn gekomen en bij toepassing van een gestimuleerde biologische in situ sanering op chloorkoolwaterstoflocaties waar organische hulpstoffen worden geïnjecteerd. De in grondwater voorkomende waterstofconcentraties kunnen dan sterk afwijken van de (dicht bij) evenwichtssituatie. Ze worden bepaald door de in situ waterstofproductie en consumptiesnelheden, die onder andere weer afhangen van het type organische stof en de snelheid van infiltratie. Een eerste conceptueel model voor een kinetische beschouwing van dit soort situaties is besproken in de hoofdstukken 2 en 3. Deze methode is verder niet uitgewerkt en toegepast in deze fase van het project.

In fase 1 zijn zowel de empirische relatie als de methode met thermodynamische berekeningen gebruikt voor interpretatie van gemeten waterstofconcentraties. De thermodynamische berekeningen zijn uitgevoerd voor de waterstofconsumerende processen, dat wil zeggen de redox- en dechloreringsprocessen, waarbij voorlopig is aangenomen dat voor alle reacties een minimale energiebehoefte van 5 kJ/mol geldt. Grenswaarden van waterstof zijn niet berekend; er is volstaan met de weergave van een thermodynamische grootte, de Gibbs-energie. Indien deze meer negatief is dan -5 kJ/mol wordt geconcludeerd dat de condities gunstig zijn om dat proces op dat meetpunt te laten verlopen.

Methode voor on-site bemonstering en analyse van waterstof

Aangezien waterstof een klein molecuul is, diffundeert het door vrijwel alle kunststoffen; opslag en transport naar het laboratorium is daarom niet wenselijk. Tevens is waterstof zeer reactief. Waterstof moet daarom op locatie worden gemeten. Dit is mogelijk met behulp van een gaschromatograaf uitgerust met een 'reduction gas detector' (RGD). Met behulp van de 'gas-stripping' methode wordt waterstof uit het grondwater in de gasfase overgebracht. Na het verversen van het grondwater in de peilbuis wordt met een debiet van minimaal 500 ml per minuut grondwater door een 'gasbulb' van 250 ml gepompt. In de 'gasbulb' wordt vervolgens 20 ml stikstofgas gebracht. Na 25 minuten worden uit de gasfase vier monsters op de GC-RGD geanalyseerd. Na vijf minuten worden wederom vier monsters uit diezelfde gasfase genomen en geanalyseerd op de GC-RGD. Wanneer de waarde minder dan 5 % afwijkt van de gemeten waarde bij 25 minuten wordt aangenomen dat er een evenwicht is bereikt. Voor het omrekenen van de waterstofconcentratie in de gasfase naar de concentratie in de waterfase wordt gebruik gemaakt van de Henry-coëfficiënt. De kosten van een waterstofanalyse op locatie bedragen, inclusief reis- en materiaalkosten, ongeveer 450 gulden per meetpunt. De kosten zijn exclusief concentratieprofielplots en interpretatie van de gegevens.

Waterstofmetingen op vier locaties: uitvoering en interpretatie

De volgende vier locaties zijn onderzocht:

- drie locaties die verontreinigd zijn met chloorkoolwaterstoffen en in mindere mate met BTEX, namelijk: de locatie Rademarkt te Groningen, het DAF-terrein te Eindhoven, het NS-revisieterrein te Tilburg;
- één stortplaats, namelijk Banisveld te Boxtel.

Naast waterstofmetingen zijn op deze locaties op alle meetpunten ook de macrochemie, de redoxpotentiaal, het DOC-gehalte en (indien relevant) de concentraties aan chloorkoolwaterstoffen en afbraakproducten (PER, TRI, CIS, VC en etheen) bepaald. Aldus zijn vier redoxidentificatiemethoden toegepast:

- **redoxpotentiaalmeting** (de Eh-methode);
- interpretatie van **macrochemische** parameters (de macrochemische methode);
- interpretatie van **waterstofmetingen** door middel van de empirische relatie tussen de redoxconditie en waterstofconcentraties (de empirische methode);
- interpretatie van **waterstofmetingen** door middel van thermodynamische berekeningen op basis van waterstofconcentraties en macrochemische parameters (de thermodynamische methode).

Uit de concentraties van de CKW's en afbraakproducten is de mate van in situ dechlorering afgeleid in termen van de dechloreringsindex. Ook de mate waarin de dechlorering thermodynamisch gezien gunstig is werd berekend aan de hand van gemeten concentraties. De mate van dechlorering is vergeleken met de redoxkarakteristiek en andere parameters zoals DOC-gehalte en het voorkomen van co-contaminanten zoals BTEX.

Rademarkt te Groningen

Redoxkarakterisatie

Op deze locatie is een grote overeenkomst gevonden tussen de redoxkarakterisering door middel van de macrochemische, de empirische en de thermodynamische methoden. Eh-resultaten geven geen consistent beeld. Een hoge variatie aan redoxcondities (variërend tussen aëroob en methanogeen) is aangetroffen, overeenkomstig een eerdere karakterisering in het kader van NOBIS-onderzoek. De meerwaarde van de thermodynamische methode blijkt uit het feit dat in redoxovergangszones kan worden aangetoond dat de condities voor verschillende redoxprocessen gunstig zijn.

In situ dechlorering

Berekeningen tonen aan dat dechlorering onder alle condities thermodynamisch gunstig is. Op de Rademarkt-locatie is geen overall relatie gevonden tussen de dechlorering en de waterstofconcentratie. Wel is bij de meetpunten met een relatief hoge waterstofconcentratie (> 2 - 3 nM) ook de meest volledige dechlorering gevonden. Op deze locatie ligt het DOC-gehalte relatief laag (5 - 25 mg DOC/l) en er kan een correlatie tussen de waterstofconcentratie en de DOC-concentratie worden aangetoond.

DAF-terrein te Eindhoven

Redoxkarakterisatie

Op deze locatie is een grote mate van overeenkomst gevonden tussen redoxkarakterisering door middel van de empirische en de thermodynamische methoden. Er is een grote discrepantie gevonden tussen dit resultaat en de redoxpotentiaalmetingen en de macrochemische analyse; deze laatste leveren geen consistent redoxpatroon op voor de verschillende bodemlagen van de locatie. Een beperkte variatie aan redoxcondities (in hoofdzaak variërend tussen ijzerreducerend

en methanogeen) is aangetroffen. De meerwaarde van de twee waterstofmethoden blijkt uit dit genoemde resultaat: alleen op deze manier kunnen redoxpatronen worden afgeleid.

In situ dechlorering

Op deze locatie is geen overall relatie gevonden tussen de dechloreringsindex en de waterstofconcentratie. Over de gehele pluim worden afbraakproducten van dechlorering gevonden ongeacht de waterstofconcentratie. Op punten met hoge waterstofconcentraties blijkt ook het DOC-gehalte verhoogd, of blijken co-contaminanten zoals BTEX en dichloorethaan aanwezig; dit zijn stoffen die als substraten voor waterstofproductie en/of elektronendonor voor dechlorering kunnen fungeren.

NS-revisieterrein te Tilburg

Redoxkarakterisatie

Op deze locatie is een grote mate van overeenkomst gevonden tussen alle methoden voor redoxkarakterisering, ofschoon door de beperkte set aan meetpunten duidelijke redoxpatronen moeilijk zijn af te leiden en niet alle methoden volledig kunnen worden toegepast. De empirische waterstofmethode geeft hier het meest consistente beeld en correspondeert met de Eh-resultaten. Een variatie aan redoxcondities (variërend tussen nitraatreducerende en methanogene condities) is aangetroffen.

In situ dechlorering

Op deze locatie zijn indicaties gevonden dat er een relatie is tussen de dechloreringsindex en de waterstofconcentratie. Wederom is bij de meetpunten met een relatief hoge waterstofconcentratie (> 2 - 3 nM) ook de meest volledige dechlorering gevonden. Op die punten blijkt het DOC-gehalte sterk verhoogd (tot ca. 100 mg DOC/l) ten gevolge van additionele verontreiniging met minerale olie en BTEX; dit zijn stoffen die als substraten voor waterstofproductie en/of elektro-nendonor voor dechlorering kunnen fungeren.

Banisveld te Boxtel

Redoxkarakterisatie

Op deze locatie zijn grote verschillen gevonden tussen redoxkarakterisering door middel van de macrochemische, empirische en de thermodynamische methoden. De thermodynamische methode wordt hier gezien als de methode die het meest betrouwbare en volledige redoxpatroon oplevert. De empirische waterstofmethode levert hier geen consistent beeld, mogelijk ten gevolge van de hoge in-flux van DOC en andere redoxspecies, waardoor niet-evenwichtssituaties kunnen zijn ontstaan. Ook de macrochemische methode geeft geen consistent beeld. Eh-metingen zijn niet uitgevoerd.

Vergelijking van de karakterisering door middel van waterstof voor vier locaties

Redoxkarakterisatie

De bruikbaarheid van de waterstofmeting voor redoxkarakterisatie blijkt uit de samenvattende tabel (zie tabel I). Zowel de empirische methode als de thermodynamische methode (ook wel partiële evenwichtsbenadering genoemd) leveren in drie van de vier gevallen een consistent redoxpatroon, in tegenstelling tot de meer traditionele redoxkarakteriseringmethoden op basis van macrochemische analyse en redoxpotentiaalmetingen. De empirische waterstofmethode lijkt een goed instrument voor een eerste screening van de redoxsituatie op een locatie. Daarna kan een meer gedetailleerd bemonsterings- en analyseprogramma worden uitgevoerd om zo op basis van macrochemische parameters en waterstofmeetwaarden door middel van de thermodynamische methode een meer complete en meer accurate redoxkarakteristiek vast te stellen.

Tabel I. Overzicht van de bruikbaarheid van de verschillende redoxidentificatiemethoden. De gegevens zijn gebaseerd op de metingen die zijn uitgevoerd op de vier locaties.

locatie	redoxpotentiaal	macrochemie	empirische methode	partiële evenwichtsbenadering
Rademarkt	-	+	+	++
DAF	+/-	-	+	++
SBNS	+/-	+	+	(*)
Banisveld	(**)	-	-	++

- geen consistent beeld
- + consistent beeld, identificatie van dominante processen
- ++ consistent beeld, identificatie van gelijktijdig optredende processen
- (*) niet genoeg data
- (**) niet gemeten

In situ dechlorering

Op de locaties is niet altijd een volledige correlatie gevonden tussen de waterstofconcentratie en de mate van dechlorering (de dechloreringsindex). Wel is geconstateerd dat bij de meetpunten met een relatief hoge waterstofconcentratie (> 2 - 3 nM) op alle locaties ook de meest volledige dechlorering wordt gevonden. Op die punten blijkt het DOC-gehalte verhoogd en/of andere co-contaminanten aanwezig die als substraten voor waterstofproductie en/of elektronendonor voor dechlorering kunnen fungeren. Er is een relatie gevonden tussen het DOC-gehalte en de waterstofconcentratie; met toenemende DOC-gehalten neemt de H₂-concentratie toe.

Conclusies en aanbevelingen

Het doel van fase 1 van dit project was de bruikbaarheid van waterstofmetingen als aanvullende redoxkarakteristiek en als graadmeter voor de intrinsieke dechloreringsconditie van de bodem in de praktijk op een aantal locaties te toetsen.

Waterstofmetingen blijken een sterk toegevoegde waarde bij de redoxkarakterisering te hebben. Waterstofmetingen in grondwater kunnen worden gebruikt bij een eerste snelle on-site screening van de redoxsituatie. Hierbij wordt voor de interpretatie gebruik gemaakt van de empirisch vastgestelde relatie tussen de waterstofconcentratie en de redoxtoestand. Voor een meer nauwgezette redoxkarakterisering is naast meten van de waterstofconcentraties ook een bepaling van macrochemische parameters noodzakelijk. Een interpretatie van deze gegevens met thermodynamische berekeningen geeft het meest complete redoxpatroon. Wanneer bij een redoxkarakterisering op basis van macrochemie of redoxpotentiaal de waterstofmetingen worden weggelaten, lijkt dit vaak een onvolledige en inconsistente redoxpatroon op te leveren.

Er zijn sterke aanwijzingen dat waterstof een bruikbare parameter kan zijn voor het inschatten van de in situ dechloreringsconditie. De mate waarin dit ook werkelijk het geval is, is nog niet volledig duidelijk. Er is voor één van de vier locaties een relatie tussen de dechlorering en de waterstofconcentratie gevonden. Op alle locaties is geconstateerd dat in aanwezigheid van voldoende DOC, BTEX, minerale olie, dichloorethaan, enzovoorts, de waterstofconcentraties relatief hoog zijn (> 2 - 3 nM) en dat in die gevallen ook een hoge mate van dechlorering optreedt. Mogelijk is het noodzakelijk dat de waterstofconcentratie boven een grenswaarde van enkele nM uit moet komen om de dechlorering voldoende snel en volledig te laten plaatsvinden.

Aanbevolen wordt in een eventuele vervolgfase van het project, conform het oorspronkelijk projectplan (= fase 2), de relatie tussen DOC, waterstofproductiesnelheid, waterstofconcentraties, snelheid en mate van dechlorering en andere parameters nader te onderzoeken. Dit kan door middel van multiparameteranalyse van de data die in fase 1 van dit project gegeneerd zijn.

Tevens kunnen data uit aanpalende projecten worden gebruikt. Op korte termijn staan metingen gepland bij Rademarkt, Zaltbommel, Tilburg en Eindhoven en circa 10 stortplaatsen.

In aanvulling worden laboratoriumexperimenten met natuurlijk sediment en grondwatermonsters aanbevolen om ook nog bestaande thermodynamische en microbiologische kennisvelden te kunnen ophelderen. Zo zijn grensconcentraties voor productie van waterstof uit natuurlijke organische koolstof en voor dechloreringsprocessen belangrijke kennisleemten waar nader onderzoek zich op zou moeten richten. De verwachting is dat na afronding van dat onderzoek de waterstofmeting als een bewezen en volwassen methode voor de vaststelling van redox- en dechloreringscondities kan worden gebruikt.

Leeswijzer

In hoofdstuk 2 wordt een theoretische overzicht gegeven over de basisbeginselen van de redoxreacties in grondwatersystemen en de waterstofproductie en -consumptie in anaërobe ecosystemen. Hoofdstuk 3 behandelt het dechloreringsproces en de rol van waterstof in deze. Een aantal verschillende redoxidentificatiemethoden wordt besproken in hoofdstuk 4, waarna in hoofdstuk 5 een methode wordt besproken hoe de gemeten waterstofconcentratie te gebruiken bij de bepaling van de mate van dechlorering. In hoofdstuk 6 wordt een algemeen karakterisatieschema gegeven en uitgelegd.

Een procedure om waterstof te meten in het veld is weergegeven in hoofdstuk 7. Tevens wordt stap voor stap uitgelegd hoe in het veld moet worden gemeten, welke apparatuur hiervoor nodig is en wat de kosten zijn.

Vier locaties zijn in dit onderzoek gemeten en worden één voor één behandeld in achtereenvolgens hoofdstuk 8, 9, 10 en 11. In hoofdstuk 12 worden deze verschillende locaties met elkaar vergeleken. In hoofdstuk 13 worden de conclusies van het onderzoek, inclusief de aanbevelingen weergegeven.

SUMMARY

Hydrogen as indicator for in situ redox condition and dechlorination

Intrinsic and stimulated natural biodegradation of chlorinated hydrocarbons (like per- and trichloroethylene) are important in in situ remediation of groundwater polluted with these compounds. The objective of this project was to assess the usefulness of on-site hydrogen measurements for characterising the in situ redox status and dechlorination condition in contaminated subsurfaces. At three sites contaminated with chlorinated solvents and in one landfill plume hydrogen was measured in combination with a characterisation of the redox chemical parameters and chlorinated solvent degradation products. Various methods were used for interpretation of these data, and the different results were compared and evaluated.

The study showed that redox characterisation using on-site determined hydrogen concentration data has a beneficial cost-performance ratio compared to traditional approaches, methods solely based on macro chemical parameters or redox potential measurements. With hydrogen measurements, a fast on-site screening of the redox situation can be performed. In a next step, a detailed and consistent redox characterisation can be achieved by measuring hydrogen and other groundwater chemical parameters at selected sampling points and using a thermodynamic interpretation method. In a number of cases, omitting hydrogen measurements was shown to lead to an inconsistent picture of the redox status at the site. Hence, redox characterisation by using hydrogen appears to be cheaper and better than traditional methods solely based on groundwater chemistry or redox potential measurements.

Measuring hydrogen in groundwater is probably also useful for the assessment of the in situ dechlorination condition. At in situ hydrogen concentrations higher than 2 nM a relatively high degree of dechlorination was observed. At various sites, the presence of either sufficient DOC, BTEX, mineral oil, or 1,2-dichloroethane, appeared to correspond to elevated hydrogen concentrations and higher degrees of dechlorination. A clear relation could not yet be established, however. Although these first results are promising, gathering more data and conducting research on a number of knowledge gaps are both required for assessing the possibilities and the limits of hydrogen measurement as an indicator for the in situ dechlorination condition.

Below, an executive summary of the work is given.

Executive summary

Intrinsic and stimulated natural biodegradation of chlorinated hydrocarbons (like per- and trichloroethylene, PCE and TCE) are important for in situ remediation of groundwater polluted with these compounds. Remediation of sites polluted with PCE and TCE is in most cases complex and costly. One possibility to reduce the costs of these remediations is to use - and when necessary stimulate - the natural degradation processes. For this it is required to assess the subsurface condition with respect to intrinsic dechlorination, i.e., the degree of dechlorination already occurring, the required redox potential needed for reductive or oxidative dechlorination, the presence of sufficient electron donors/en⁻acceptors, and the presence of a microbial population, sufficiently adapted to degradation of the contaminants.

On-site measurement of hydrogen concentrations in groundwater can possibly be used as an indicator for the degree of intrinsic dechlorination in a contaminated aquifer. In addition, hydrogen measurements can give a more complete redox characterisation which is important in an effective use of the natural and enhanced bioremediation.

The research was planned in two phases. The first phase is reported here, and aims at developing a method for on-site measurements, the testing of the method under practical conditions, review and development of the theoretical fundamentals required for interpretation of hydrogen concentration data, measuring hydrogen at four different sites, and the interpretation and evaluation of the obtained results. Phase two, not yet conducted, should provide a multi-site analyses in which a statistic correlation between hydrogen concentration and other parameters (i.e. DOC, co-contaminants, groundwater chemistry) can be identified.

This report covers phase I, performed between may '98 and march '99.

Objective

This study aims to assess the usefulness of hydrogen measurements for determining the intrinsic dechlorination condition and the redox status of a contaminated aquifer.

Workplan phase 1

The following parts have been performed:

1. Development and evaluation of a fundamental scientific knowledge basis for the interpretation of hydrogen measurements for redox characterisation and natural degradation potentials.
2. Installation of equipment for analysis and sampling and development of a method for on-site sampling and analyses of hydrogen.
3. Performance of hydrogen measurements on a number of sites and the interpretation on the basis of formulated scientific/technical framework (1) in terms of hydrogen as indicator for the redox condition and the intrinsic biodechlorination status.

In this project, four locations are studied:

- three sites contaminated with chlorinated solvents, and to a lesser extend with BTEX, namely:
 - the Rademarkt site, Groningen;
 - the DAF site, Eindhoven;
 - the NS train maintenance facility, Tilburg.
- one landfill, contaminated with heavy metals, aromatics and chlorinated hydrocarbons, namely:
 - the Banisveld site, Boxtel.

The results of the hydrogen measurements are evaluated per site and correlated to other redox parameters and the dechlorination index. In addition the results of the four sites are compared and the added value of hydrogen measurements to already existing methods is evaluated. The findings are in short reported below.

Development of scientific knowledge basis for the interpretation of hydrogen measurements

In the theoretical chapters two and three is analysed and described what the role of hydrogen can be in the in the subsurface occurring redox processes which are in practical all situations catalysed by micro-organisms. Hydrogen is an intermediate in the natural fermentation of organic material in the subsurface. The formed hydrogen reacts with help of micro-organisms with other soil and groundwater constituents. Hydrogen is an electron donor, transfers electrons to these components, which are electron acceptors. These can be natural electron acceptors like oxygen, nitrate, iron(III), sulphate, en carbon dioxide, or pollutants like PCE, TCE and other chlorinated compounds that are dechlorinated through this process (see fig. I).

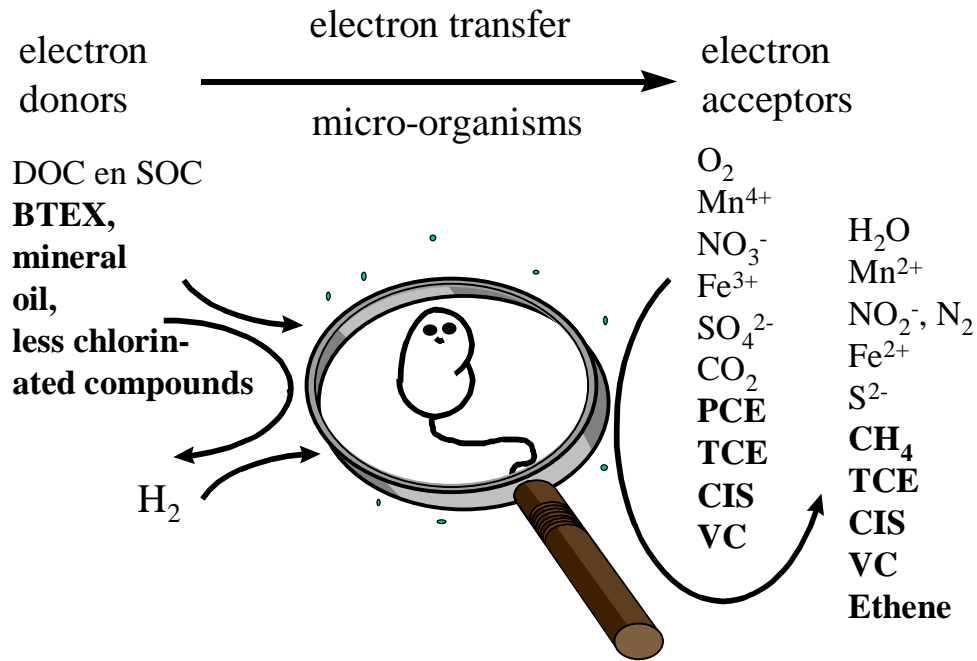


Fig. I. Role of hydrogen and micro-organisms in the subsurface redox processes.

The concentration level of hydrogen in groundwater is determined by a complex network of inter-related processes in which on hydrogen is produced out of organic matter and hydrogen is consumed by reaction with soil and groundwater constituents. In this study an inventory was made on possible mechanisms involved, and which biological and chemical parameters may be relevant. For a detailed description the reader is referred to the chapters two and three in the report. Here, the main issues are presented.

Subsurface system close to equilibrium

In a natural non-disturbed soil system, processes are often close to equilibrium and the hydrogen concentration corresponds to the redox condition of that specific environment. For such environments, studies have been reported in literature, where with laboratory experiments *ranges* of hydrogen concentrations were established and empirically related to the pre-installed redox condition. This **empirical approach** can thus be used for the interpretation of on-site measured hydrogen concentrations in terms of a redox condition, and provides a practical tool for redox characterisation (see fig. II).

With this empirical approach it is important to correct for the actual subsurface temperature. In this report indications for temperature correction are given.

The measured values of hydrogen can also be interpreted by combined use of hydrogen concentrations and macro chemical parameters in a **thermodynamic calculation** (in this report also referred to as the partial equilibrium approach). In this way it can be established which redox processes are favourable, i.e. *can* occur at that certain sampling point. This is possible for all subsurface redox processes and also for dechlorination reactions.

Steady-state hydrogen range

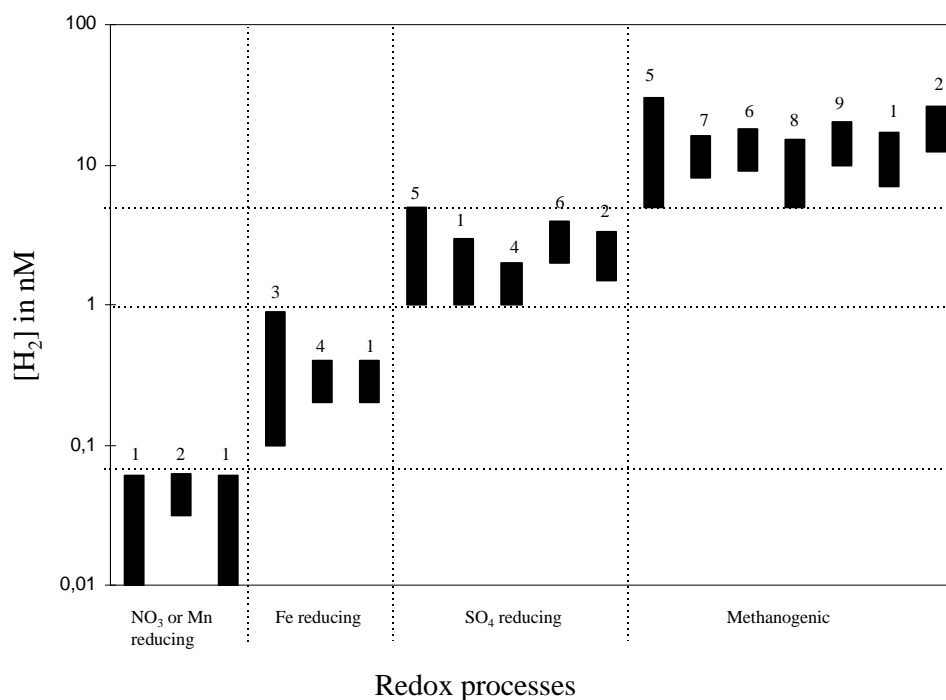


Fig. II. Overview of steady-state H₂-concentrations related to different redox processes at standard temperature (25 °C). The values are from the following references: 1: [Lovley and Goodwin, 1988]; 2: [Hoehler et al., 1998]; 3: [Chapelle and Lovley, 1992]; 4: [Lovley and Philips, 1987]; 5: [Vroblesky and Chapelle, 1994]; 6: [Lovley et al., 1982]; 7: [Lovley and Klung, 1982]; 8: [Goodwin et al., 1988]; 9: [Conrad et al., 1987].

The advantage of the thermodynamic approach is that it is a more standard method, independent of site specific criteria. From the inventory it became clear that a number of knowledge gaps still exist, and major non-validated assumptions still have to be made in this method. This makes it not (yet) possible to consider the redox status picture obtained with the thermodynamic approach as the 'true' picture for that site; it should be considered as the 'best estimate' that can be get at this moment. One important unknown in-input parameter is the minimal energy that microorganisms need to gain out of specific redox- and dechlorination reactions in order to survive. Only very general values for this parameter could be found in the literature. A standard value for this minimal energy yield of 5 kJ/mol is used for all thermodynamic calculations performed in this study. For the dechlorination reactions especially, but possibly also for all the other biologically mediated redox processes, the true value may be higher. For dechlorination reactions in which hydrogen is the main electron donor, a higher minimal energy need of the microbial dechlorinating population will be reflected in a higher hydrogen threshold concentration below which dechlorination will not occur.

A subsurface system far out of equilibrium

Interpretation of hydrogen concentrations in a subsurface system brought out of equilibrium is much more complex. This can occur at landfill sites where large quantities of organic carbon are fed into the groundwater system and at chlorinated solvent sites where organic carbon substrates are injected for remediation purposes. Then, the hydrogen concentrations do not reflect the current redox situation and are determined by the dynamics of hydrogen production/consumption velocities. A first conceptual model for such a kinetic evaluation for this type of situations is discussed in chapters 2 and 3. This method is not further employed in this

phase of the project, since significant additional research efforts are needed to further develop the scientific basis for such interpretations.

Methods applied

In this phase 1, the empirical relation as well as the thermodynamic calculation method was used for the interpretation of measured hydrogen concentrations. The thermodynamic calculations were conducted for the hydrogen consuming processes, i.e., the redox- and dechlorination processes, with the assumption that the minimal energy need for all reactions is 5 kJ/mol. Threshold values for hydrogen were not calculated. The thermodynamic quantity, the Gibbs energy was determined for each redox process, and when this quantity was found to be more negative than -5 kJ/mol, it is concluded that the conditions are favourable for that process at that specific monitoring point.

Method for on-site sampling and analyses of hydrogen

Hydrogen is a small molecule and diffuses through almost all polymeric substances. In addition, hydrogen is a reactive species and concentrations may change rapidly. Therefore, sample storage and transport to the laboratory for analyses is not recommended. Hence, hydrogen should be measured on-site to minimise risks on artefacts. This is possible by using a gas chromatograph equipped with a reduction gas detector (RGD). With a 'gas liquid equilibrium' method, hydrogen is transferred from the groundwater to the gas phase, sampled and analysed. Groundwater is pumped from a well at a minimum rate of 500 ml per minute and lead through a 'gasbulb' of 250 ml. In the 'gasbulb' 20 ml nitrogen gas is injected. After 25 minutes four gas phase samples are taken and subsequently analysed with GC-RGD and the average value is notated. After five minutes again four samples are taken, analysed, and averaged. When the deviation of the two average values is less than 5 % the average value is assumed to correspond to the in situ hydrogen concentration. For calculation of the water phase hydrogen concentrations from the gas phase concentrations Henry's law is used. The costs of a hydrogen analyses, including travel and material costs, is 450 guilder per sampling point. These costs are for a minimum of 10 samples per day and exclude concentration profile plots and interpretations i.e., with the thermodynamic calculation.

Hydrogen measurements on four sites: data presentation and interpretation

In addition to hydrogen measurements also macro chemical parameters, redox potential, DOC contents and concentrations of chlorinated solvents and degradation products (PCE, TCE, cis-DCE, VC, and ethene) were determined. Thus four redox identification methods have been applied:

- **redox potential** determination (the Eh-method);
- interpretation of **macro chemical** parameters (the macro chemical method);
- interpretation of **hydrogen measurements** through the empirical relation between redox condition and hydrogen concentrations (the empirical method);
- interpretation of **hydrogen measurements** with thermodynamic calculations on the basis of hydrogen concentrations and macro chemical parameters (the thermodynamic method).

From the concentrations of chlorinated hydrocarbons and degradation products the degree of in situ dechlorination was deduced, in terms of a dechlorination index. Also it was evaluated with measured concentrations which dechlorination reactions are thermodynamically favourable. The degree of dechlorination was compared to redox characteristics and to the parameters like DOC content and the presence of co-contaminants like BTEX.

Rademarkt site at the city of Groningen

Redox characterisation

On this site, redox characterisation using the macro chemical, the empirical and the thermodynamic method yielded comparable results. The Eh-results were inconsistent with those of other three methods. A high variation in redox conditions was found, varying between aerobic and methanogenic conditions and which is in agreement with a former characterisation, performed in NOBIS research in 1996. The added value of the thermodynamic approach was demonstrated by the fact that this method indicated that in redox transition zones various redox processes are favourable, i.e., can occur simultaneously.

In situ dechlorination

Calculations showed that all dechlorination steps are thermodynamically favourable under the various conditions identified at the site. There was no overall relation between degree of dechlorination and hydrogen concentration. At a few sampling points, hydrogen was present at elevated concentrations (> 2 - 3 nM), and at these points also the most complete degree of dechlorination was observed. On this site, DOC values are rather low (5 - 25 mg DOC/l) and a significant correlation between hydrogen concentration and DOC concentration was found.

DAF site at the city of Eindhoven

Redox characterisation

On this site a large degree of agreement was found between the redox characterisation through the empirical and through the thermodynamic method. A large discrepancy was found between these results and the redox potential measurements and the macro chemical method. These two methods yielded an inconsistent redox pattern. A limited variation in redox conditions was found, i.e. iron-reducing to methanogenic conditions. The added value of the two hydrogen based methods was demonstrated by the fact that only in this way a consistent redox picture could be deduced.

In situ dechlorination

On this site, no overall relation between dechlorination index and hydrogen concentrations could be found. Distributed over the entire plume degradation products were found irrespective of the hydrogen concentrations. High hydrogen concentration corresponded to high DOC levels, or co-contaminants such as BTEX and dichloroethane. These compounds are substrates for hydrogen production and can function as electron donor for dechlorination.

The NS train maintenance site at the city of Tilburg

Redox characterisation

On this site a large degree of agreement was found between all methods for redox characterisation. Due to a limited data set, a fully clear redox pattern could not be deduced and not all methods could be applied to all sampling points. The empirical method did give the most complete and consistent picture and corresponded well with the Eh-results. Redox conditions identified varied between nitrate-reducing and methanogenic conditions.

In situ dechlorination

On this site, indications were found for a relation between dechlorination index and the hydrogen concentration. Again, high hydrogen concentrations (> 2 - 3 nM) appeared to correspond to the highest degree of dechlorination, and high DOC levels (up to 100 mg DOC/l) due to co-contaminants as mineral oil and BTEX. Substances that have the potential to act as substrates for hydrogen production and/or electron donor for dechlorination.

Banisveld, a landfill site at the city of Boxtel

Redox characterisation

On this site large differences were found between the results of the various redox identification methods, i.e., the macro chemical, the empirical, and the thermodynamic method. The thermodynamic method is considered as the best estimate. The empirical method and the macro chemical method did not yield a consistent picture. Possibly the large discrepancies are the result of the high in-flux of DOC and other redox species into the landfill plume resulting in non-equilibrium conditions.

Comparison of redox and dechlorination results for the four sites

Redox characterisation

The usefulness of hydrogen measurements for redox characterisation is depicted in the following table (see table I).

Table I. Overview of the usefulness of the various redox identification methods. These results are based on measurements and evaluations performed for the four sites.

site	redox potential (Eh) method	macro chemical method	empirical method, hydrogen	thermodynamic method, hydrogen en macrochemistry
Rademarkt	-	+	+	++
DAF	+/-	-	+	++
SBNS	+/-	+	+	(*)
Banisveld	(**)	-	-	++

- no consistent redox picture
- + consistent redox picture, identification of dominant redox processes
- ++ consistent redox picture, identification of specific redox processes that can occur simultaneously
- (*) incomplete data
- (**) not measured

Both the empirical method and the thermodynamic method (also referred to as the partial equilibrium approach) provide in three out of four cases a consistent redox pattern, in contrast with the more traditional redox characterisation methods based on macrochemistry or redox potential measurements. The empirical method appears to be a very well instrument for a first screening of the redox situation at a site. After this a more detailed sampling and analysis programme can be conducted in which hydrogen concentrations and macrochemistry are determined and then can be interpreted with thermodynamic calculations, thus leading to a more complete and adequate redox picture.

In situ dechlorination

A relation between DOC level and hydrogen concentration was found: increasing DOC levels corresponded to increasing concentration of hydrogen. In contrast, a clear correlation between hydrogen concentration and degree of dechlorination (dechlorination index) was not found. However, it was observed that, sampling points with a relatively high hydrogen concentration (> 2 - 3 nM), also showed high degrees of dechlorination. At these sampling points, the DOC level was relatively high or co-contaminants like BTEX, 1,2-dichloroethane, or mineral oil were present. These compounds may reduce the redox potential since they are electron donors, and possibly also fuel the dechlorination as direct electron donors or through the production of hydrogen. More data gathering and research is required to further elucidate these relations and processes.

Conclusions and recommendations

The objective of phase 1 of the project is to test the usefulness, added value, of hydrogen measurements as redox identification tool and as an indicator for the intrinsic dechlorination condition of a subsurface system at four sites.

Hydrogen measurements have a strongly added value for redox characterisation. Hydrogen measurements in groundwater can be used for a fast and rough on-site screening of the redox situation, using the empirical relation between hydrogen concentration and the redox condition for interpretation. After this, a more thorough redox characterisation can be conducted following a more focussed sampling and analyses programme and by determining hydrogen concentrations and macro chemical parameters. Interpretation using the thermodynamic calculations gives the most complete and best estimate of the redox situation. Omitting hydrogen based redox characterisation, and only using traditional macro chemical or redox potential identification methods leads in a number of cases to incomplete or inconsistent redox patterns.

A number of indications were found that hydrogen can also be used as an indicator for the in situ dechlorination condition. To what extent this really is the case, is not yet clear. In one out of four sites a relation between dechlorination index and hydrogen concentration was found. On all sites, elevated levels of DOC, BTEX, mineral oil, 1,2-dichloroethane, etc., were accompanied with high levels of hydrogen concentrations (> 2 - 3 nM) and high degrees of dechlorination. Possibly, the hydrogen concentration needs to exceed a certain threshold value (of a few nM?) in order to sufficiently promote reductive dechlorination. Also from the theoretical evaluation, the existence of a hydrogen threshold concentration due to inefficient energy conservation of dechlorinating micro-organisms was identified as an hypothesis to be tested.

It is recommended to pursue with phase 2 of the project as was stated in the original project plan, i.e. to investigate the relation between DOC levels, hydrogen production velocities, hydrogen concentrations, velocity and degree of dechlorination and other parameters. This can be done through a multiparameter analyses of existing field data and new field data currently gathered during site characterisation. In addition new data from typically non-equilibrium situations can be used from monitoring programmes of active in situ remediations currently performed at Rademarkt, Zaltbommel, Tilburg, and Eindhoven and characterisation of about ten landfill sites. In addition, laboratory research with natural sediment and groundwater samples is recommended to elucidate still existing thermodynamic and microbiological knowledge gaps. The threshold concentrations for production of hydrogen from natural organic carbon resources and for hydrogen consumption for redox and dechlorination processes are important knowledge gaps for further research. It is expected that after that research, hydrogen measurements can be used as a fully proven method for redox identification and a scientifically based approach to establish in situ dechlorination conditions.

Reading guide

In chapter two a theoretical review is given on basic principles of redox reactions and hydrogen production and consumption in anaerobic groundwater ecosystems. The third chapter discusses the dechlorination process and the possible roles hydrogen has in this process. A number of redox identification methods are discussed in chapter four. In chapter five a method is presented how measured hydrogen concentrations can be used in the assessing the dechlorination condition. A general characterisation scheme which is used for the four studied sites, is presented and explained in chapter six. A description of procedure for on-site hydrogen measurements and equipment needed is given in chapter seven. Also the costs per hydrogen measurement are presented there. Four sites have been characterised according to the scheme, and the data and interpretations are presented and discussed in chapters eight to eleven. Chapter twelve includes a four site evaluation, and chapter 13 contains the conclusions and recommendations.

CHAPTER 1

INTRODUCTION

Worldwide, many sites are contaminated and pose a potential threat to the well-being of man, flora and fauna. Chlorinated hydrocarbons are among the most frequently occurring contaminants in soil and groundwater. The use of intrinsic degradation processes (the most significant process of natural attenuation) is becoming more and more an option for the control and restoration of contaminated sites. The hydrogen concentration in groundwater may be an important parameter in assessing the natural attenuation (NA) potential at contaminated sites, especially those polluted with chlorinated compounds. The feasibility of NA as remedial option of chlorinated solvents can be assessed through the following phases [Wiedemeier et al., 1997; Rijnaarts et al., 1998; Sinke et al., 1998]:

1. Collecting indicative information on NA

Gathering information on indicators and appropriate conditions for intrinsic degradation are often used at first instance and address the following parameters:

- *Parent compounds and degradation products*
Concentrations of parent compounds and formed degradation products indicate the degree at which intrinsic dechlorination has occurred.
- *Redox condition and electron acceptors*
The in situ redox condition and concentrations of chemical species corresponding to electron-accepting processes.
- *The in situ electron donor activity*
(Organic) electron donors are driving the reductive dechlorination of chlorinated solvents and other chlorinated compounds. Different types of organic carbon sources can serve as intrinsic electron donors, namely naturally present dissolved organic carbon (DOC) or co-contaminants such as BTEX, petroleum hydrocarbons, or other organics.

2. Quantification of NA

This is determined by a documented loss of mass of contaminant over time and space in a contaminant plume.

This last phase is performed at each site at which monitored NA has been accepted as the most feasible pollution control approach. In many cases (new sites, complex situations) NA cannot yet be completely quantified, and one starts with phase 1. Sinke et al. [1998] have developed (and are further developing) a decision tool to proceed through these steps in an efficient way.

Where the assessment of the parent compounds and degradation products is relatively straightforward, the other two parameters often form a bottleneck, for which measurements of hydrogen concentrations in groundwater may offer a solution:

- *Redox condition and electron acceptors*
Redox conditions as measured with an electrode, have been proven to give often unreliable results in practice. Hydrogen measurements may provide a more reliable method and may be useful for a first on-site quick scan prior to a more detailed characterisation. Interpretation of groundwater chemistry is also hampered by uncertainties. Chemical species consumed and formed by electron-accepting processes can disperse through the site after the reactions took place. As a consequence, interpretation in terms of electron-accepting processes that occur at a specific monitoring point (and the related condition for intrinsic degradation) remains difficult. Hydrogen concentrations may give a better and more complete picture of the redox condition, of the potentially occurring electron-accepting processes, and therefore also of the basic in situ condition for intrinsic degradation of the organic pollutants present.

- *The in situ electron donor activity*

The amount of in situ electron donor which drive the reductive dechlorination of chlorinated compounds has been found to be important for intrinsic dechlorination. Different types of organic carbon sources can serve as intrinsic electron donors, namely naturally present DOC or co-contaminants as BTEX, petroleum hydrocarbons, or other organics. The in situ activity of these compounds and mixtures with respect to releasing reduction equivalents needed for dechlorination is difficult to assess. The hydrogen concentration in groundwater may be indicative for this activity, and may form a simple lump sum parameter to qualify the intrinsic dechlorination condition.

Thus measuring hydrogen concentrations may provide a way to improve the assessment of the NA potential at contaminated sites. However, the theoretical fundamentals, the practical possibilities and limitations, and the adequate tools for interpretation are either unclear or described fragmented in the international literature. The aims of this project were therefore the following:

- to systematically review the theoretical fundamentals and assumptions underlying the role of hydrogen in in situ redox and dechlorination processes;
- to review and further develop the methods of measuring and interpreting hydrogen concentrations;
- to test the usefulness of the hydrogen concentration as a redox characterisation and/or intrinsic dechlorination parameter at four different sites in the Netherlands;
- to indicate the potential use of the hydrogen concentration as monitoring tool for NA and enhanced natural dechlorination.

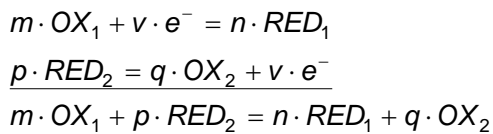
These aims are addressed in the various chapters of this report. Chapter 2 in this report gives a theoretical overview of the basic principles of redox reactions in groundwater systems, hydrogen production and consumption in anaerobic ecosystems and gives conceptual models that describe the reactions in soil and groundwater in which hydrogen takes part. Chapter 3 describes dechlorination processes and the role of hydrogen in it. Chapter 4 describes some different redox identification methods. Chapter 5 discusses different ways to use hydrogen as a method to evaluate dechlorination and in chapter 6, a general scheme for characterisation is explained. A description of the operation procedure for hydrogen measurements in the field is described in chapter 7. Including a step by step guideline and an overview of the equipment needed to measure hydrogen in the field. In chapter 8, 9, 10 and 11, four different case studies are reported according to the general characterisation scheme. In chapter 12 these results are compared to each other. Chapter 13 gives conclusions about the hydrogen measurements in relation to redox characterisation and in situ reductive dechlorination, including the outlook and recommendations for future application and optimisation.

CHAPTER 2

HYDROGEN: REDOX AND MICROBIAL INTERACTIONS

2.1 Basic principles of redox reactions in groundwater systems

Organic matter in soils and aquifers is subjected to decomposition. Decomposition can be seen as a microbially mediated redox reaction. The organic matter is oxidised and donates electrons through various intermediary compounds to terminal electron acceptors, which subsequently become reduced. Redox reactions can be described as the combination of two reduction half reactions:



Where OX_1 is the terminal electron acceptor (oxidator) and RED_2 the electron donor (reductor), e^- is an electron and v , m , n , p and q are constants.

The terminal electron acceptors most often found in natural systems are oxygen, nitrate, Mn(IV), Fe(III), sulphate, and carbon dioxide (see table 1). Organic compounds such as quinone moieties of humic acids or other organic acids (e.g. acetate, fumarate, caffeate) are also known to be used as electron acceptor by anaerobic micro-organisms. Because the contribution of organic compounds to the electron flow in anaerobic groundwater systems is still unknown their role will not be further considered in the present report. Among the inorganic electron acceptors there is a well-defined sequence which is related to the amount of energy which is gained from the redox reaction. Micro-organisms tend to oxidise organic matter by using the electron acceptor that provides the most energy [Stumm and Morgan, 1981]. Due to this sequence of terminal electron-accepting processes, distinct zones may develop in the subsurface, marking the domination of particular electron acceptors.

Table 1. Relevant half reactions for electron acceptor utilisation in natural systems. This table is not a complete overview, but rather covers the most common reactions in natural systems. Half reactions are normalized to one electron (e^-).

half reactions		
$\frac{1}{4} O_2(g) + H^+ + e^-$	=	$\frac{1}{2} H_2O$
$\frac{1}{5} NO_3^- + \frac{6}{5} H^+ + e^-$	=	$\frac{1}{10} N_2(g) + \frac{3}{5} H_2O$
$\frac{1}{2} NO_3^- + H^+ + e^-$	=	$\frac{1}{2} NO_2^- + \frac{1}{2} H_2O$
$\frac{1}{8} NO_3^- + \frac{5}{4} H^+ + e^-$	=	$\frac{1}{8} NH_4^+ + \frac{3}{8} H_2O$
$\frac{1}{2} MnO_2(s) + 2 H^+ + e^-$	=	$\frac{1}{2} Mn^{2+} + H_2O$
$Fe(OH)_3(s) + 3 H^+ + e^-$	=	$Fe^{2+} + 3 H_2O$
$\frac{1}{8} SO_4^{2-} + \frac{5}{4} H^+ + e^-$	=	$\frac{1}{8} H_2S(g) + \frac{1}{2} H_2O$
$\frac{1}{8} SO_4^{2-} + \frac{9}{8} H^+ + e^-$	=	$\frac{1}{8} HS^- + \frac{1}{2} H_2O$
$\frac{1}{8} HCO_3^- + \frac{9}{8} H^+ + e^-$	=	$\frac{1}{8} CH_4(g) + \frac{3}{8} H_2O$
$\frac{1}{8} CO_2(g) + H^+ + e^-$	=	$\frac{1}{8} CH_4(g) + \frac{1}{4} H_2O$
$H^+ + e^-$	=	$\frac{1}{2} H_2(g)$

Under steady-state conditions where the supply and demand of electron acceptors and donors is in balance, one microbially mediated redox reaction will predominate within a distinct zone [Ponnamperuma, 1972; Froelich et al., 1979; Reeburgh, 1983]. However, in many cases redox processes are not in steady-state and change within time and in space [Vroblesky and Chapelle, 1994]. Moreover, oftentimes several redox processes take place simultaneously.

2.2 Microbiological hydrogen production and consumption

2.2.1 Anaerobic food web

The decomposition of organic matter in anaerobic ecosystems is brought about by a complex microbial food web [Conrad, 1989; Schink, 1997]. The dominant primary sources of organic material in most natural ecosystems include polysaccharides (e.g. cellulose, hemicellulose, pectin, chitin), lignin, fulvic and humic acids, protein, lipids and nucleic acids, derived from plants and lower animals. These complex polymers are broken down into simpler molecules in a stepwise process, mediated by the concerted action of different specialised microbial species. The anaerobic microbial communities can be arranged in a general scheme comprising (at least four) specific 'trophic' or 'functional' groups (see fig. 1). The metabolism of these groups is linked through excretion and consumption of degradation products. In a first step the high-molecular organic compounds are depolymerised by hydrolytic and fermenting bacteria yielding oligomers, e.g. peptides and disacchrides, and monomers, e.g. sugars, amino acids, purine and pyrimidine bases, aromates and long chain fatty acids. The oligo- and monomers can be utilised as direct growth substrates by respiring bacteria which use nitrate, Fe^{3+} , Mn^{4+} , sulphate or CO_2 as electron acceptor. Alternatively, the monomers may be fermented to short chain fatty acids, aromates, alcohols, CO_2 and hydrogen. The fatty acids, alcohols and aromates are further oxidised to acetate and CO_2 by obligate proton-reducing bacteria which use H^+ as electron acceptor, forming H_2 . Because this step is energetically unfavourable and - for thermodynamic reasons, see below - only proceeds at low H_2 -concentrations, the obligate proton-reducing bacteria live in syntrophic association with H_2 -consuming anaerobes. Thus the oxidation of the final products of the anaerobic food chain requires the activity of anaerobic H_2 -consuming bacteria, particularly nitrate-reducing, metal-reducing, sulphate-reducing, methanogenic or homo-acetogenic bacteria. These hydrogenotrophic micro-organisms use H_2 as an energy source and catalyse the transfer of electrons from hydrogen to one of the electron acceptors, nitrate, manganese(IV), iron(III), sulphate or bicarbonate (see table 1), and maintain the H_2 -concentration below the thermodynamic *maximum* permitted for the activity of the obligate proton-reducing bacteria. The turnover of H_2 between hydrogen producers and consumers has been termed interspecies hydrogen transfer [Iannotti et al., 1973; Gottschalk, 1986].

Overall the process of organic matter mineralisation in anaerobic ecosystems thus yields CO_2 , water and reduced electron acceptor molecules. Obviously, the specific pathways of carbon and electron flow through the food web, and the related activity of specific microbial communities depends on many factors, including :

- The prevailing physical and chemical conditions (pH, temperature, groundwater flow, soil matrix structure etc.).
- The quality of the organic matter. Aged organic matter usually consists of more refractory carbon, such as an increased amount of humic acids. Especially in deeper soils (older groundwater) this may be important because the reactivity (i.e. availability as electron donor for dechlorination) may be limited.
- The (bio)availability of inorganic electron acceptors, which strongly controls the kinetics of the reduction processes in soil.
- The presence of organic and inorganic contaminants. These may either act as electron donor or acceptor, or inhibit microbial activity due to toxicity effects.
- The presence or absence of specific microbial species or communities with unique biodegradation capacities.

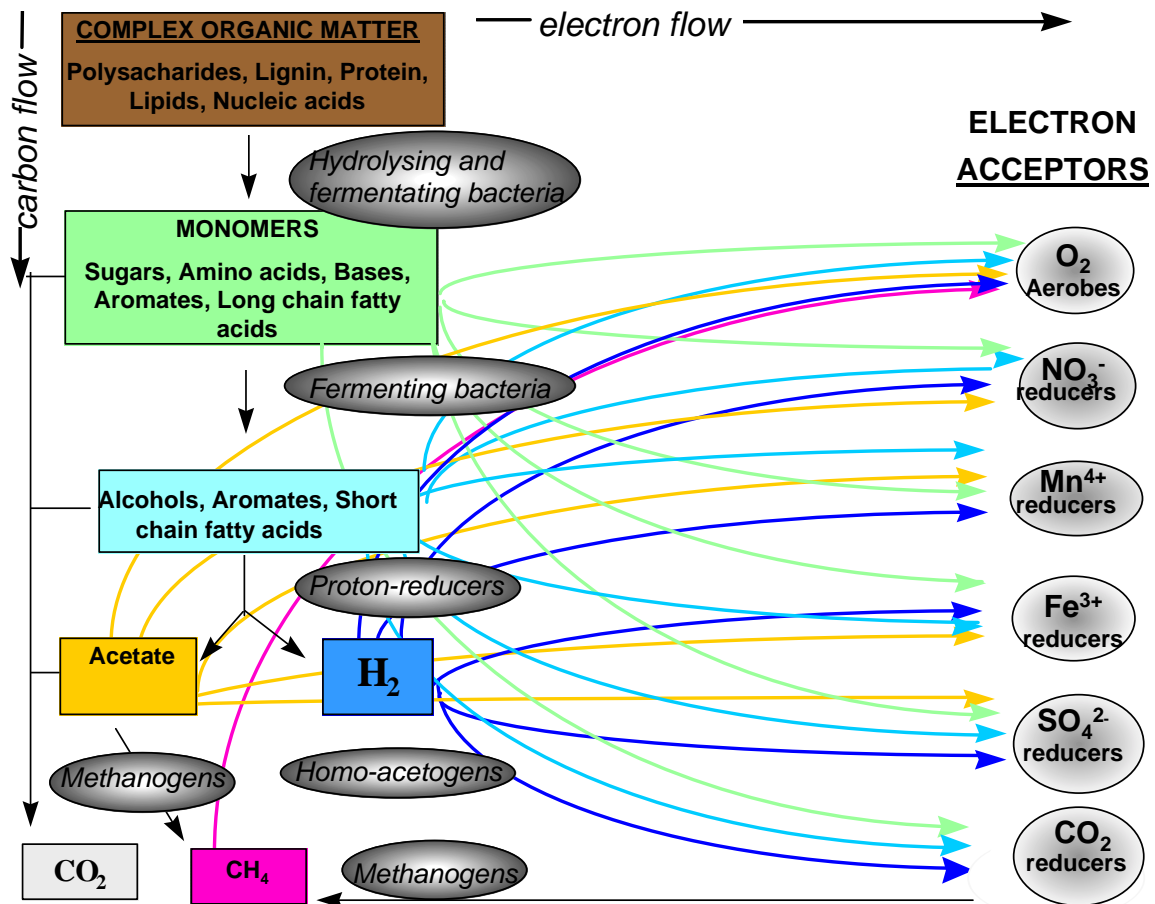


Fig. 1. Microbial food web for degradation of organic matter, showing a carbon flow between the different trophic groups (vertically) and an electron flow from the trophic groups to an electron acceptor (horizontally).

2.2.2 Control of H₂-concentration in groundwater

The concentration of molecular hydrogen in the groundwater reflects the flow of carbon and electrons from electron donor substrates to electron acceptors through the anaerobic microbial food web. Hydrogen is continuously produced and consumed during different stages of the decomposition of organic matter (see fig. 1). The most important H₂-producing bacteria are the fermenters and the obligate proton reducers. Hydrogen production by the fermenting bacteria is relatively independent on its prevailing concentration. This is caused by the fact that oxidation of the substrates used by the fermenters (e.g. glucose, fructose, lactate) is thermodynamically feasible, even at high p_{H₂} (hydrogen pressure). In contrast, oxidation of the substrates of the obligate proton-reducing bacteria (e.g. alanine, phenol, butyrate, benzoate, propionate) is energetically unfavourable, particularly at high hydrogen concentrations. Hence, different electron donor substrates each have certain '*maximum threshold H₂-concentrations*' associated with their degradation. For example, the maximum allowed H₂-concentration for oxidation of the following substrates decreases from saturation to less than 0.1 nM in the order: glucose, fructose > lactate > methanol > alanine > ethanol > phenol > glycolate > butyrate > benzoate > propionate > acetate. Obviously, the specific maximum hydrogen concentrations depend also on the prevalent in situ conditions - particularly the temperature and pH - surrounding the H₂-producing microbial communities [Schink, 1997].

The hydrogenotrophic bacteria use different terminal electron acceptors that all compete for hydrogen as an energy source for growth. Interestingly, these different H₂-oxidising populations

have different affinities for H₂, and in addition, require distinct *minimum threshold H₂-concentrations* for growth. Generally, micro-organisms mediating an energetically favourable terminal electron-accepting process are strong competitors for H₂, because they consume H₂ at high rates, have high growth yields, and are capable of growing at relatively low H₂-concentrations. Consequently they reduce the H₂-concentration to lower levels than the H₂-thresholds required for organisms catalysing energetically using less favourable electron acceptors [Lovley and Goodwin, 1988; Lovley et al., 1982]. Experimental evidence indicates that indeed micro-organisms mediating less favourable reactions are out-competed for H₂ by bacteria mediating energetically more favourable reactions [Conrad, 1996; Cord-Ruwisch et al., 1988; Schink, 1997]. A general order of ranking of bacteria with decreasing affinity for H₂ is as follows: aerobes, nitrate-reducers, manganese-reducers, iron-reducers, sulphate-reducers and methanogens (see table 2).

Table 2. Some redox reactions mediated by hydrogen consuming bacteria.

reaction		
2 H ₂ + O ₂	=	2 H ₂ O
5 H ₂ + 2 NO ₃ ⁻ + 2 H ⁺	=	N ₂ + 6 H ₂ O
H ₂ + NO ₃ ⁻	=	NO ₂ ⁻ + H ₂ O
4 H ₂ + NO ₃ ⁻ + 2 H ⁺	=	NH ₄ ⁺ + 3 H ₂ O
H ₂ + MnO ₂ + 2 H ⁺	=	Mn ²⁺ + 2 H ₂ O
H ₂ + 2 FeOOH + 4 H ⁺	=	2 Fe ²⁺ + 4 H ₂ O
4 H ₂ + SO ₄ ²⁻ + H ⁺	=	HS ⁻ + 4 H ₂ O
4 H ₂ + HCO ₃ ⁻ + H ⁺	=	CH ₄ + 3 H ₂ O

As a result, the syntrophic degradation of organic substrates takes place within a specific range of H₂-concentrations. The upper and lower threshold H₂-concentrations allowing growth of a syntrophic consortium depend on the particular electron donor/electron acceptor substrate combination utilised by the bacteria (see fig. 2).

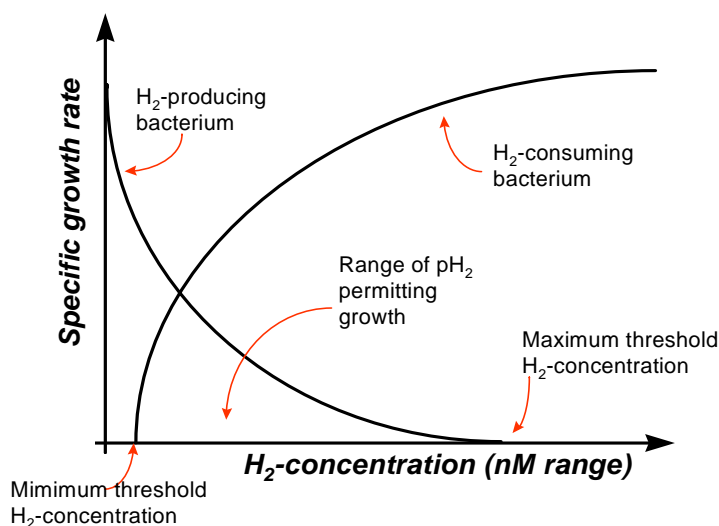


Fig. 2. Influence of the H₂-concentration on the specific growth rate of a H₂-producing and a H₂-consuming bacterium. Obviously, the precise shape and position of the curves depends on the growth properties of the bacteria and the electron donor and acceptor substrates utilised.

Altogether, the H₂-concentration in groundwater systems is controlled by both the kinetic properties of the H₂-producing and the H₂-consuming bacteria, as well as by the thermodynamic constraints of mediated redox reactions.

The *kinetics* are especially important in *non-steady-state* situations. For example, upon a sudden input of electron donor substrates in an anaerobic system, the H₂-formation will increase up to the maximum rate catalysed by the enzymes

Thermodynamic

Fig. 3. Cartoon-like impression of processes affecting the H₂-concentration in groundwater. The level of H₂ depends on the supply of electron donor substrates and its conversion to H₂ and the H₂-flow to electron acceptors. In this particular example sulphate-reducing conditions prevail, and dominate over iron-reducing, manganese-reducing, nitrate-reducing and oxygen-reducing conditions.

2.2.3 *Conceptual model of H₂-production and H₂-consumption*

The complex scheme of hydrogen production and consumption within the anaerobic food web can be translated into a conceptual model (see fig. 4). The H₂-concentration is lifted by the activity of fermenting and proton-reducing bacteria (V₁ and V₂). The H₂-concentration is pulled down (V₄) by the activity of hydrogen consumers among which are the dechlorinating micro-organisms. The net H₂-level in the groundwater is the resultant of hydrogen production and consumption rates between thermodynamically imposed maximum and minimum concentrations (steady-state hydrogen threshold). Consumption and production rates and threshold values vary among the numerous micro-organisms involved. The availability of inorganic electron acceptors for H₂-oxidation is additionally determined by their reduction mediated by bacteria using other electron donors such as organic matter or its degradation products (V₃, V₅ and V₆).

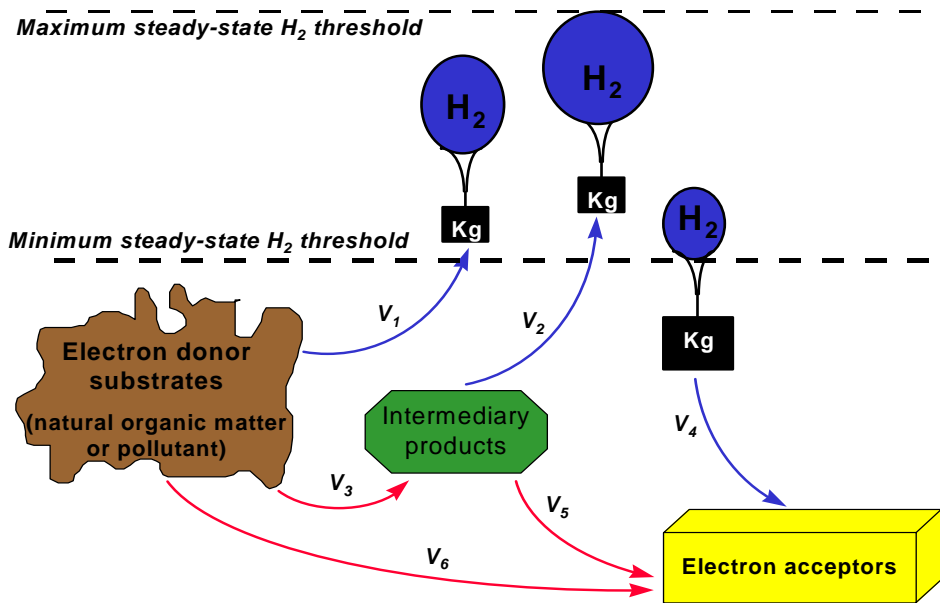


Fig. 4. Conceptual model of H_2 -production and H_2 -consumption in anaerobic groundwater systems. The arrows indicate the flow of electrons.

The conclusion is, that in a natural groundwater system a multitude of processes, micro-organisms, and thermodynamic constraints determine the hydrogen concentration. No model can be expected to give a complete deterministic description of all these phenomena. Hence, a more empirical evaluation of these relations between hydrogen and electron transfer processes is warranted.

HYDROGEN: DECHLORINATION PROCESSES

3.1 Biotransformation of organic pollutants

Biodegradation by bacteria is the most important mechanism for the removal of organic pollutants from groundwater systems. Micro-organisms catalyse the transformation of pollutants through two principally different mechanisms: metabolism and co-metabolism [Alexander, 1985; Gerritse et al., 1995; Gerritse et al., 1997, Rijnaarts et al., 1998]. During metabolic biodegradation the organic pollutants are used by the micro-organisms for the generation of energy and/or biomass (see fig. 5). In contrast, co-metabolic transformations are 'by-reactions' of enzymes which are actually intended for microbial growth on natural substrates.

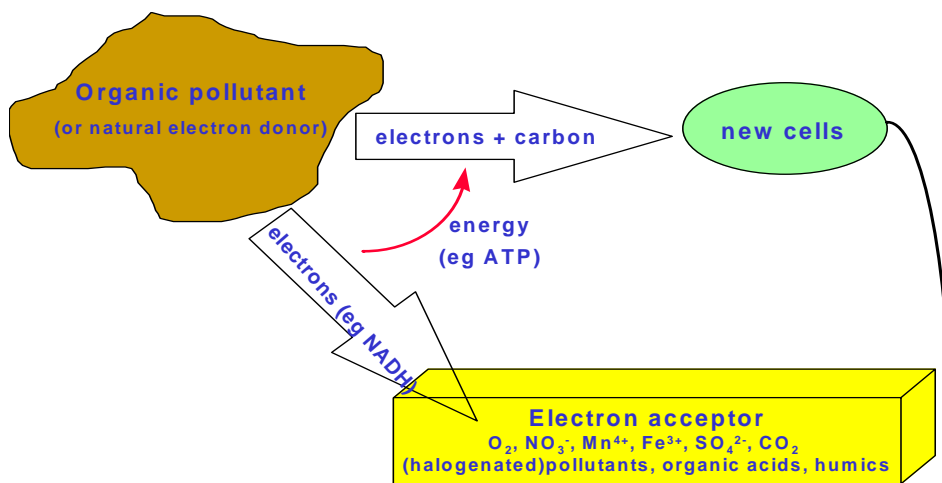


Fig. 5. Metabolic degradation of organic pollutants (after [Rittmann et al., 1993]).

The organic compounds can be degraded either as an electron donor or as an electron acceptor.

In case the organic pollutant is used as an *electron donor*, it is oxidised, e.g. to CO_2 or acetate. The discharged electrons are either excreted as H_2 , and/or organic fermentation products, or transferred within the organism (e.g. as NAD(P)H or FADH) to an electron acceptor (e.g. O_2 , NO_3^- , Fe^{3+} , Mn^{4+} , SO_4^{2-} , or CO_2). Examples of pollutants that can be oxidatively degraded (can function as electron donor) are: BTEX-aromatics, mineral oil constituents, polyaromatic hydrocarbons (PAHs) some low halogenated aliphatics (e.g. dichloromethane, 1,2-dichloroethene, vinylchloride) and aromatics (e.g. chlorobenzene, monochloro- and monofluorobenzoates).

Other pollutants like chlorinated organic compounds can be used as *electron acceptors*. This reductive dechlorination process is called 'halorespiration' in case the microbes involved conserve the energy released via electron transport and synthesis of ATP (oxidative phosphorylation). To fuel reductive dechlorination the micro-organisms require an electron donor substrate (see fig. 6). The electron donors known to be used by halorespiring bacteria are molecular hydrogen, short chain fatty acids (e.g. acetate, lactate, butyrate), ethanol, amino acids (e.g. serine), or reduced inorganic compounds such as sulphide.

Fig. 6. Use of electron donors and acceptors by dehalorespiring *Desulfitobacterium* species.

The presence and availability of the various electron acceptors strongly controls the structure and the activity of the local microbial communities and related pathways, rates and extents of pollutant biodegradation. Generally, in an 'oxidised environment' (e.g. aerobic or denitrifying conditions) oxidative degradation of BTEX, oil, PAHs and mono-chlorinated compounds proceeds readily, whereas reductive transformations are relatively slow and incomplete. The opposite is true for a strongly 'reduced environment' (e.g. sulphate-reducing or methanogenic conditions) favouring reductive dechlorination of PCE, TCE, and other highly chlorinated pollutants (PCBs, chlorobenzenes, HCH, DDT, dioxins) and restraining oxidative biodegradation. In general, for organic compounds that contain halogen-, sulphony-, nitro- or azo-groups, the biotransformation characteristic changes with decreasing substitution number, from 'preferentially degraded through reduction' (many groups per molecule) to 'preferentially degraded through oxidation' (one or few groups per molecule).

3.2 Reductive dechlorination of chloroethenes

Reductive dechlorination is the most important mechanism for the transformation of a wide spectrum of chlorinated aromatic and aliphatic pollutants. In fact, for poly-chlorinated compounds as tetrachloroethene (PCE), tetrachloromethane, hexachloroethane, hexachlorobenzene and PCBs containing more than six chlorines it is the only biotransformation mechanism known [Mohn and Tiedje, 1992; Rijnaarts et al., 1998]. This process occurs under anaerobic conditions and proceeds faster and more complete when the environment becomes more reduced.

Reductive dechlorination of PCE involves the stepwise replacement of chloride atoms for protons (see fig. 7). Thus PCE is subsequently reduced to trichloroethene (TCE), cis-1,2-dichloroethene (DCE), vinylchloride (VC), and ethene. [Vogel and McCarty, 1985; Bruin et al., 1992; DiStefano et al., 1991; Freedman and Gossett, 1989].

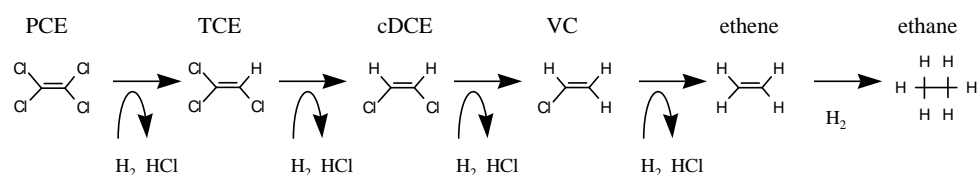


Fig. 7. Reductive dechlorination of chloroethenes with H₂ as electron donor.

Anaerobic bacteria that use PCE or TCE as terminal electron acceptor have recently been isolated and include: *Dehalospirillum multivorans*, *Dehalobacter restrictus*, *Desulfitobacterium* species, *Dehalococcus ethenogenes* and *Desulfuromonas chloroethenica* [Gerritse et al., 1996; Gerritse et al., 1999]. These halo-respiring bacteria were capable of dechlorination-dependent growth at relatively high rates and indicate the great microbial potential for natural and enhanced remediation of chloroethene-contaminated aquifers [Gerritse et al., 1998]. In reduced (sulfido- or methanogenic) environments reductive dechlorination of PCE and TCE usually proceeds at relatively high rates and has been demonstrated at lower rates under nitrate- and iron-reducing conditions. During reductive dechlorination of PCE and TCE the lower chlorinated ethenes, particularly DCE and VC, often accumulate. Apparently, their reduction is often more restrained. Several explanations have been proposed for this phenomenon:

- i) reductive dechlorination of DCE and VC is a co-metabolic process, not providing an energy and electron source required for the development of a VC/DCE-degrading microbial community;
- ii) dechlorinating enzymes hav

reaction		
PCE + H ₂	=	TCE + Cl ⁻ + H ⁺
TCE + H ₂	=	DCE + Cl ⁻ + H ⁺
DCE + H ₂	=	VC + Cl ⁻ + H ⁺
VC + H ₂	=	ethene + Cl ⁻ + H ⁺
ethene + H ₂	=	ethane

The presence of natural electron acceptors often inhibit the dechlorination process. Particularly O₂, NO₃⁻ and Mn⁴⁺ are known to inhibit dechlorination of chloroethenes. Some studies indicated that PCE dechlorination was retarded and less complete in the presence of iron oxides or sulphate. However, other investigations do not confirm these observations. Although the influence of electron donors and acceptors on the reductive dechlorination process is complex and not well understood, some mechanisms involved have been identified:

1. Competition for electron donors between dechlorinating and non-dechlorinating bacteria (see below).
2. Reduction of alternative electron acceptors with H₂ as donor. In this way H₂ reduces the redox potential of the environment, and optimises the conditions for reductive dechlorination.
3. Preference of halorespiring bacteria for natural instead of chlorinated electron acceptors. When alternative electron acceptors are available, halorespiring bacteria can shift the electron flow from PCE or TCE to for example nitrate or sulfoxy-anions (see fig. 6 [Gerritse et al., 1996; Gerritse et al., 1997; Gerritse et al., 1999]).

In soil and groundwater systems there is a strong competition for electron donor substrates between dechlorinators and *non*-dechlorinating bacteria that use natural acceptors, especially O₂, NO₃⁻, Mn⁴⁺, Fe³⁺, SO₄²⁻, or CO₂. Particularly use of O₂, NO₃⁻ and Mn⁴⁺ as electron acceptor is energetically favourable, and the bacteria respiring with these electron acceptors have a high affinity for electron donors (including H₂) and high growth yield. They appear capable of out-competing other anaerobic including dechlorinating bacteria.

An additional important factor controlling the competition for hydrogen between different terminal electron acceptors utilising bacteria was shown to be the 'threshold' for hydrogen uptake (see chapter 2). Bacteria using nitrate, manganese or iron in the terminal electron-accepting process can grow at very low hydrogen concentrations (< 0.2 nM). Such concentrations are too low for the growth of bacteria mediating less favourable terminal electron-accepting processes as sulphate- or carbon-dioxide reduction which require at least 1 nM H₂.

From a thermodynamic point of view, reductive dechlorination is a very favourable process. The Gibbs energies that are involved in dechlorination reactions remain negative even at extremely low hydrogen concentrations (< 0.01 nM). This suggests that dechlorinators should in theory be able to compete successfully with methanogens, sulphate-, iron-, manganese- and nitrate-reducing bacteria. Indeed, laboratory studies indicated that dechlorinators can use hydrogen at lower levels than methanogens [Smatlak et al., 1996; Fennell et al., 1997; Yang and McCarty, 1998]. In the presence of chloroethenes the dechlorinators maintained steady-state hydrogen levels around 2 nM and out-competed the methanogens. In methanogenic batch cultures the steady-state hydrogen concentration was significantly higher, around 11 nM, which is in line with other studies. This lower threshold H₂-value of 2 nM observed for dechlorination is in the range of the minimum hydrogen concentration required by sulphate- or iron-reducing bacteria (see fig. 9, chapter 4). These threshold hydrogen concentrations appeared independent on the type of electron donor used [Yang and McCarty, 1998].

Obviously the precise value of these threshold H_2 -concentrations depends on environmental factors as pH and temperature. Nevertheless, threshold H_2 -concentrations observed for dechlorination are considerably higher than expected on the basis of thermodynamic calculations which suggest a similar value as for nitrate reduction i.e. < 0.05 nM. This discrepancy may be explained by the fact that dechlorinators are not as efficient at capturing the energy available from hydrogen oxidation as bacteria mediating 'natural' redox reactions and operate at very low Gibbs energies [Yang and McCarty, 1998; Smatlak, 1995]. In contrast, thermodynamic calculations indicate that the available energy for methanogenesis that is taking place at the steady-state (critical) hydrogen concentration is close to the reported threshold Gibbs energy for ATP production.

This is significant because competition effects among different terminal electron-accepting processes appear of particular importance for the extent to which dechlorination of PCE takes place. The observation that DCE and VC often appear the bottleneck in the complete reductive dechlorination process can be understood in case PCE- and TCE-dechlorinating bacteria would have a considerably lower threshold for H_2 than DCE and VC dechlorinators. The fact that bacteria respiring with H_2 as electron donor and PCE and TCE as acceptor are frequently isolated, whereas anaerobes capable of respiring with and DCE or VC have not been described seems to approve this possibility. However, detailed research on the H_2 -levels during dechlorination of the different chloroethenes is needed to confirm this hypothesis.

Various experiments indicate that reductive dechlorination of chloroethenes is restrained not only at very low but also at relatively high H_2 -concentrations. It appears that in cultures in which H_2 -levels are relatively high, most of the H_2 is consumed by methanogenic bacteria. This may be explained by competitive exclusion of dechlorinators by methanogens at high hydrogen concentrations. Such a mechanism is likely in case the methanogens would have significantly higher H_2 uptake-capacity or growth rate on H_2 . An alternative explanation may be the direct inhibition of the dehalogenating activity of dechlorinators at high H_2 -concentrations. Indeed, such inhibition was observed for 3-chlorobenzoate dehalogenation by *Desulfomonile tiedjei* and in enrichment cultures containing a PCE-dechlorinating *Desulfitobacterium* species [Gerritse et al., 1996]. Although the reasons for the apparent selective advantage of methanogens over dechlorinators at high hydrogen concentrations are still unclear, the general picture that has emerged from different studies is that the competitive strength of the dechlorinators resides within their capacity to capture H_2 at lower levels than the methanogens. Therefore, the competition between methanogens and dechlorinators can be controlled by the type supply of electron donor. Based on thermodynamic considerations a selection of primary electron donors can be made beforehand. Different electron donor substrates generate different hydrogen concentrations (see chapter 2). Substrates which have a positive Gibbs energy at high hydrogen concentrations for fermentation are probably optimal primary electron donors to stimulate dechlorination. These substrates are unable to produce high concentrations of hydrogen and will be a long term source of hydrogen. For example, the oxidation of propionate or butyrate to acetate, CO_2 and H_2 by obligate proton-reducing bacteria is only energetically favourable at H_2 -concentrations just below or close to the threshold for methanogens (< 1 nM). Therefore, methanogens cannot compete successfully with dechlorinators for the low levels of H_2 generated from propionate or butyrate oxidation. In contrast, substrates as glucose, lactate, benzoate, methanol and ethanol can be fermented at H_2 -concentrations well above the levels required for optimal growth of methanogens and the competitive advantage of dechlorinators falls away. Low levels of H_2 can also be created by limiting the supply-rate of electron donor substrates. This can for example be accomplished by slow release of electron donors for example in continuous flow systems (soil columns, chemostats, infiltration wells in aquifers) or by addition of complex or relatively 'inert', slowly degradable, compounds such as poly-lactate esters (hydrogen release compound, HRC), paper- or wood

chops, compost extract, or natural organic matter which deliver hydrogen over long periods of time [Middeldorp et al., 1998; Wu et al., 1998].

CHAPTER 4

REDOX IDENTIFICATION METHODS

4.1 Traditional methods to identify redox conditions

Several attempts have been made to develop a method to determine which redox conditions take place at a given location. The most direct way is to measure the rates of the redox reactions. Since these are very slow and difficult to measure (all phases must be considered), this option is not applicable in practice. Alternatively, redox potential measurements and macro chemical methods are currently used to indicate redox conditions.

4.1.1 *Redox potential (Eh)*

Redox potential measurements are done with an electrode (e.g. Pt-electrode) against a standard electrode of known potential. Redox potentials are measured in Volts and are directly related to the free electron concentrations. It is assumed that each terminal electron-accepting process has a characteristic redox potential range. However, this method is generally found to be of limited value [Lindberg and Runnells, 1984; Berner, 1981; Stumm and Morgan, 1981]: electrodes do not respond to many of the important redox couples, redox couples are not in thermodynamic equilibrium, and the formation of oxide precipitates on the surface of the electrode leads to analytical problems. Consequently, different redox potential ranges associated with redox processes have been reported in several literature sources (summarized by: [Lovley and Goodwin, 1988]).

4.1.2 *Macrochemistry*

The term macrochemistry will be used to indicate a redox identification method that is based on the presence of and changes in the concentrations of compounds that participate in natural redox reactions. These compounds will further on be called redox species. Redox species can either be electron acceptors (O_2 , NO_3 , $Mn(IV)$, $Fe(III)$, SO_4 , HCO_3) or end products that are formed by transformation of electron acceptors in redox reactions (NO_2 , N_2 , NH_4 , $Mn(II)$, $Fe(II)$, HS , H_2S , CH_4). In principle, each redox specie that is involved in redox processes can be used, but their performance as indicator is strongly variable. Some redox processes are more suitable under certain conditions than others, but in fact each redox specie has its own specific difficulties whi.5349 3 29 >>BD

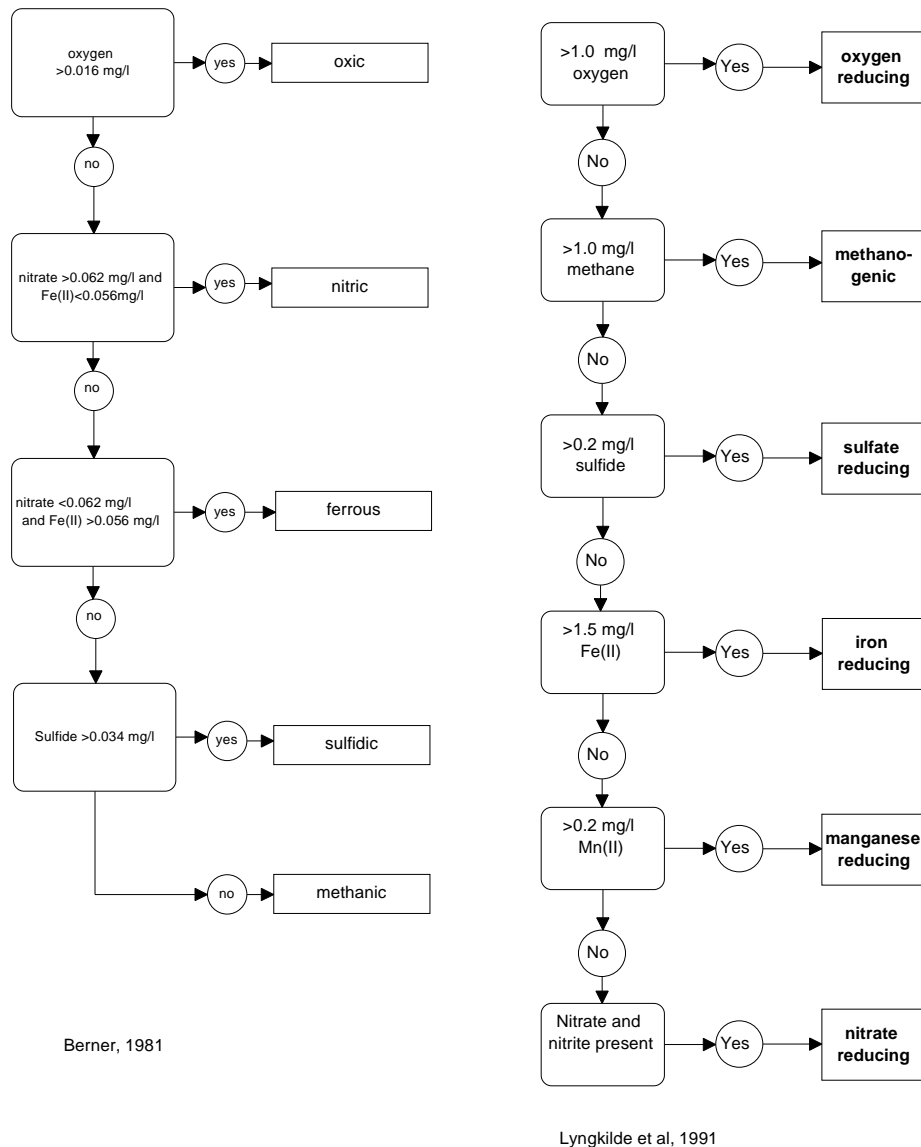


Fig. 8. Two different types of redox classifications.

4.2 Methods based on hydrogen

There are two ways in which hydrogen can be used to identify redox conditions: Comparing measured hydrogen concentrations with empirical ranges, and the partial equilibrium approach.

4.2.1 Comparison with empirical ranges

In many experiments hydrogen concentrations have been measured under (artificially produced) conditions that were demonstrated to be either nitrate-, manganese-, iron(III)-, or sulphate-reducing, or methanogenic. It appears that each redox reaction has its own specific hydrogen range, which is severely different from the hydrogen range of the other redox reactions. Therefore H_2 -concentrations can be an indicator of the terminal electron-accepting process that predominates in a given zone [Lovley and Goodwin, 1988]. H_2 is a continuously cycled intermediate product with a half-life in the order of seconds, and therefore reflects nearly instantaneous conditions at a particular well. A single analysis can, under steady-state conditions, be diagnostic of the predominant terminal electron-accepting process and concentration changes along a flow path are not required to be diagnostic of terminal electron-accepting processes. Figure 9 sum-

marises steady-state concentrations corresponding to the terminal electron-accepting processes at a standard temperature of 25 °C. Although, the values are empirically determined by different authors and under different conditions, they show to be rather consistent. Steady-state hydrogen concentrations for nitrate- and manganese-reducing and dechlorination reactions are less studied and therefore scarce.

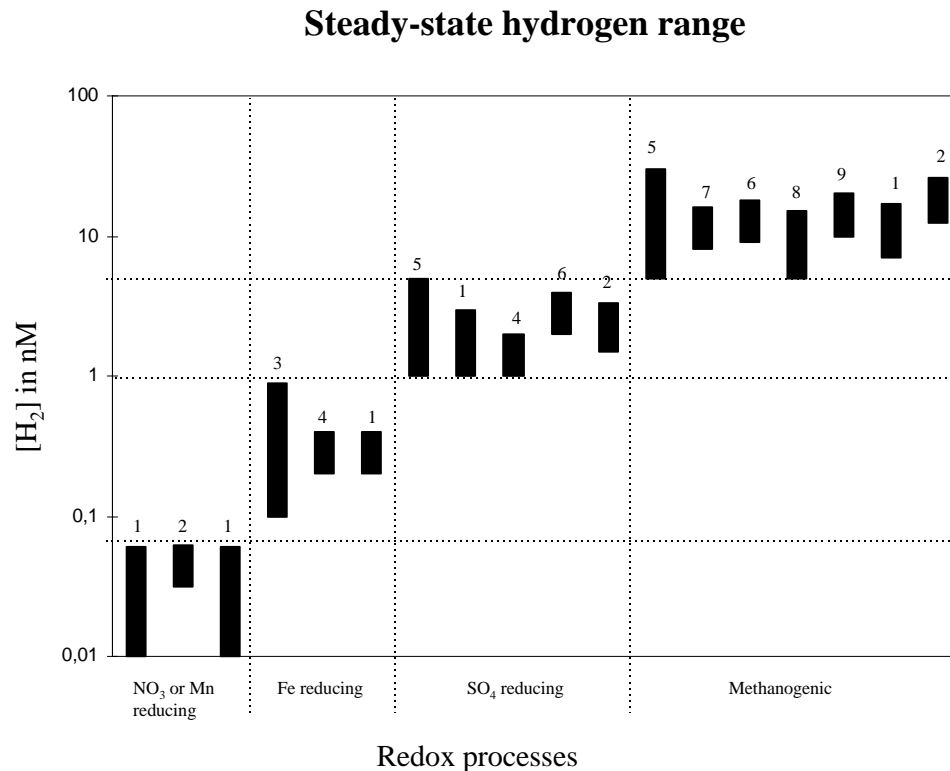


Fig. 9. Overview of ranges of steady-state H₂-concentrations (at the standard temperature of 25 °C) associated to the different redox processes. The ranges are based on the following literature: 1: [Lovley and Goodwin, 1988]; 2: [Hoehler et al., 1998]; 3: [Chapelle and Lovley, 1992]; 4: [Lovley and Philips, 1987]; 5: [Vrobesky and Chapelle, 1994]; 6: [Lovley et al., 1982]; 7: [Lovley and Klung, 1982]; 8: [Goodwin et al., 1988]; 9: [Conrad et al., 1987].

Several studies have determined the effect of temperature on the steady-state hydrogen ranges [Hoehler et al., 1998; Jakobsen et al., 1998; Schulz and Conrad, 1996; Westerman, 1994]. They all concluded that the hydrogen level is not just a function of the given redox process, but is strongly affected by the in situ temperature. A decrease in temperature leads to a decrease in the steady-state hydrogen concentration. Therefore the hydrogen ranges in figure 9 are not necessarily applicable to situations in which the temperature is significantly different from the standard temperature. A temperature between 10 and 15 °C is more common in temperate regions like the Netherlands. Table 4 indicates the hydrogen ranges that are associated with three redox processes for temperate regions. The ranges are based on data from experiments carried out in this temperature range.

Table 4. Criteria for determining redox processes by the empirical hydrogen method. These criteria are applicable in temperate regions where the groundwater is approximately 10 to 15 °C. These ranges are based on steady-state hydrogen concentrations that have empirically been determined in experiments indicated by the references.

redox condition	[H ₂] (nM) at 10 to 15 °C	based on
iron-reducing	[H ₂] ≤ 0.3	Jakobsen et al. [1998]
sulphate-reducing	0.3 < [H ₂] < 1.5	Hoehler et al. [1998] and Jakobsen et al. [1998]
methanogenic	[H ₂] ≥ 1.5	Hoehler et al. [1998], Westerman [1994] and Jakobsen et al. [1998]

In non-steady-state environments empirical hydrogen concentrations cannot be interpreted unambiguously. Terminal electron-accepting processes do not always occur in well separated zones, but to some extent they occur simultaneously, indicating that competitive exclusion is not always efficient. Terminal electron-accepting processes can co-exist when the more energetically favourable reaction is limited by electron acceptor availability. Under these conditions, the more favourable reaction can no longer maintain the hydrogen concentration below the minimum threshold necessary for hydrogen metabolism by the less favourable reaction. Additionally, a temporary increase in the rate of hydrogen production can disturb the steady-state situation, and might lead to a misinterpretation of the hydrogen concentrations. Furthermore, microzones can form another potential situation where there could be more than one electron acceptor for organic matter oxidation within a readily sampled interval. In these microzones different terminal electron-accepting processes occur compared to the bulk phase [Lovley and Philips, 1987; Lovley and Goodwin, 1988]. Thus, the existing approach to using empirical hydrogen ranges is only valid if the system studied is in a steady-state, a prerequisite that is very difficult to be certain of.

4.2.2 *Partial equilibrium approach*

The partial equilibrium approach, which was introduced by Postma and Jakobsen [1996] and Jakobsen et al. [1998], implies that fermentative hydrogen production is overall rate limiting, while terminal electron-accepting processes occur at negative Gibbs energies, close to thermodynamic equilibrium. Measured concentrations of hydrogen and redox species may be combined, through simple thermodynamic calculations (see appendix A) into an actual potential in situ energy yield, representing the potential for a given hydrogen oxidising terminal electron-accepting process. This approach is able to indicate the occurrence of concomitant terminal electron-accepting processes and to evaluate where (in the leachate plume) the different terminal electron-accepting processes can take place.

In practical terms, for each separate sampling point Gibbs energies are calculated for all relevant redox processes. The calculated Gibbs energies are subsequently used to delineate zones in which the Gibbs energy is above or below the necessary threshold (see section 2.2.2). Below this threshold (i.e. more negative) the reaction is energetically favourable and is likely to occur. Above the threshold the reaction is less favourable, but is not totally excluded to proceed. The process can still occur in stagnant subdomains if the hydrogen concentration in these is higher due to fermentation of organic matter or if hydrogen is directly transferred from fermenting to hydrogen consuming bacteria [Conrad et al., 1987]. Since different values have been reported for this threshold Gibbs, no single value can be considered to be the true threshold Gibbs energy (see section 2.2.2). Therefore it is recommended to perform a low and/or a high case scenario.

A precondition to perform this approach is the determination of the appropriate parameters. Depending on the redox reactions of interest, several redox species (both electron acceptors and final products, and of course hydrogen) must be measured in order to calculate the Gibbs energy

of those reactions (see appendix A). Apart from the concentrations of redox species also the temperature and pH are important parameters that must be measured.

In case of the iron(III)- and manganese(IV)-reducing processes, not only the concentrations of species in solution are a determining factor, but also the ones that are present as a solid phase (electron acceptors). A variety of different minerals exist in soils, each having a characteristic reactivity. The energy yield of the reaction strongly depends on the reactivity of the particular minerals that are present. The reactivity, in turn, is roughly paralleled by the stability of the minerals [Postma and Jakobsen, 1996]. Thus the stability of the minerals present determines whether iron(III) and manganese(IV) reduction are energetically favourable and likely to take place [Postma and Jakobsen, 1996].

Trivalent iron is found in several minerals, but only a few are assumed to be present in soils. Most common are iron hydroxides: α -FeOOH (goethite) and amorphous FeOOH. In some regions (e.g. the Netherlands), lepidocrocite is also present. These minerals are relatively reactive, and will be reduced first. The more stable (hydr)oxides are less reactive and yield less energy upon reduction and will be reduced in a further stage of reduction. Fe mineralogy seems to play an important role and should therefore be determined at each site in order to use the partial equilibrium approach optimally. However, this is not always achievable, and therefore best and worse case estimations can be made by assuming both stable and less stable minerals.

METHODS THAT USE HYDROGEN TO EVALUATE DECHLORINATION

The ultimate goal in this and many other projects is to obtain a tool to evaluate and to predict dechlorination processes. Here, two different methods that are based on hydrogen are discussed. The first is based on thermodynamic calculations of dechlorination reactions and is a variation on the partial equilibrium approach for redox reactions. The second method is making use of steady-state hydrogen concentrations to judge if dechlorination reactions are in a favourable range. Research on both methods is still in a very preliminary stage, but in this project a first start is made.

5.1 Thermodynamic calculations for dechlorination

Similar to the partial equilibrium approach for natural redox reactions (see section 4.2.2), thermodynamic calculations can be made to evaluate dechlorination processes. On basis of thermodynamic calculations which have been done in previous research, dechlorination reactions are considered to have very low Gibbs energies under all natural conditions. This implies that these reactions are always favourable under these conditions, when assuming that the same threshold Gibbs energy for ATP-synthesis applies as for natural redox reactions (see chapter 2). However, indications have been found by Yang and McCarty [1998] that dechlorination reactions would be less efficient than normal redox reactions. This suggests that the threshold Gibbs energy for dechlorination might be lower than for natural redox reactions. Instead of a value between -5 kJ/mol and -20 kJ/mol, a value which is much lower might be used as threshold Gibbs energy. Its exact value, though, has not been studied sufficiently and could therefore not provide a basis for this method. For this moment only thermodynamic calculations will be made, without comparing Gibbs energies to threshold values.

5.2 Steady-state hydrogen range for dechlorination

Dechlorination reactions that use hydrogen as electron donor operate optimally at a certain range of hydrogen concentrations. When hydrogen concentrations become too low, the process will be unfavourable; if they are too high, competition with natural redox processes might occur. Like natural redox processes, dechlorination processes are also expected to be able to maintain hydrogen at a steady-state hydrogen concentration which is in this favourable range. Until now, only little research has taken place on the values of this range. Data published by Yang and McCarty [1998] identify a favourable range between 2 nM and 11 nM.

In order to obtain a method to evaluate dechlorination, measured hydrogen concentrations that fall within this range will be considered favourable for dechlorination processes. In this project, this range will be further validated by comparing measured hydrogen concentrations and observed dechlorination in the field.

CHAPTER 6

GENERAL CHARACTERISATION SCHEME

The use of hydrogen as tool for the characterisation of redox conditions and its relevance for dechlorination processes is being determined at four different locations. These locations are: Rademarkt (Groningen), DAF (Eindhoven), SBNS (Tilburg) and Banisveld (Boxtel).

Since these four locations are all different types of locations as far as (geo)hydrology, the contaminated situation, and the conditions that exist are concerned, they will be discussed individually in separate chapters. In each chapter the location will be described first. Secondly, redox conditions will be characterised in different ways including traditional methods and methods based on hydrogen. Criteria that form the basis of these methods do not necessarily have to be the same and applicable for all possible locations, but can also be formulated for one particular type of location or in a site-specific way.

The redox potential will not be used as a separate tool to identify the exact redox reactions, but will be used in a comparative way to locate redox trends and to verify the results of the redox characterisation of the other methods.

For the macro chemical method, the criteria that are formulated depend on the type of location, which represents distinct background conditions and processes. In a previous NOBIS report [Sinke et al., 1998] macro chemical criteria have been formulated for the determination of the redox conditions into three distinct groups: aerobic, anaerobic and strongly anaerobic. These criteria are applicable for most types of locations in the Netherlands. In this report, the criteria for the determination of the redox conditions at the Rademarkt and SBNS site will be based on the macro chemical criteria formulated for these typical locations, however, more specific redox conditions are considered (see fig. 10). The criteria are based on the concentrations of a limited number of common redox species. Significant methane concentrations indicate that methane is produced during methanogenesis. Sulphate reduction generally occurs after iron reduction has been taken place, leading to increased divalent iron concentrations. Therefore, decreased sulphate concentrations in combination with increased divalent iron concentrations indicate sulphate reduction. The presence of oxygen and nitrate indicate oxygen and nitrate reduction, respectively. Iron-reducing conditions apply to the cases that do not fit any of the criteria mentioned above.

CH ₄ > 1 mg/l	→yes: methanogenic
↓	
SO ₄ < 1.5 mg/l	→yes: sulphate-reducing
Fe(II) > 1.5 mg/l	
↓	
O ₂ > 1 mg/l	→yes: oxygen-reducing
↓	
NO ₃ > 0.5 mg/l	→yes: nitrate-reducing
↓	
no:	iron-reducing

Fig. 10. Criteria for the determination of the redox conditions for a typical location using macro-chemistry.

The DAF and Banisveld location strongly deviate from the typical locations in terms of background concentrations. The formulated macro chemical criteria (see fig. 10) cannot form a basis for the determination of the redox conditions at these sites. Instead, distinct site-specific criteria have been formulated for these locations (see chapter 9 and 11).

Also the steady-state hydrogen concentrations associated with redox processes are expected to be different per location. Hydrogen concentrations are not considered to be a function of redox processes only, but are also affected by other local conditions (see chapter 3). For the Dutch situation, the hydrogen range in table 4 (see section 4.2.1) can be used for most of the sites. Also for the Rademarkt, DAF, and SBNS site it will provide the criteria for the empirical hydrogen method. However, for the Banisveld location, this range was found to be inadequate for the interpretation of the redox conditions (see chapter 11).

The criteria for the partial equilibrium approach on the other hand, are the same for all locations because the variability in conditions is already included in this method. For the four locations a Gibbs energy of -5 kJ/mol has been selected as criterion. This value is the highest of the range of values that has been reported in literature (see chapter 2). The reason for doing so is to be sure that no reactions that possibly occur are excluded beforehand, when the Gibbs energy of a reaction is close to the threshold. This reduces the possibility of excluding a favourable reaction. Consequently, reactions might be falsely included. However, a better estimate of the threshold value would bring partial equilibrium interpretations closer to the real situation.

All redox identification methods will be evaluated and the results will be compared in order to come to a reliable redox characterisation.

At all locations, dechlorination processes will be analysed and related to hydrogen. A comparison between dechlorination and the redox conditions according to methods based on hydrogen will be made. More direct comparisons are made between dechlorination and empirical ranges of hydrogen concentrations. Additionally, thermodynamic calculations are made for the dechlorination reactions with hydrogen as electron donor to see if they are energetically favourable. Furthermore, comparisons are made with the type of electron donor which is present.

In order to make comparisons, dechlorination has to be quantified. The chloride number (Cl#) is a useful tool to indicate the stage of dechlorination that exists at a certain part of the location. The Cl# is defined as follow:

$$\text{Cl\#} = \frac{4[\text{PCE}] + 3[\text{TCE}] + 2[\text{DCE}] + [\text{VC}]}{\sum[\text{chloroethenes}] + [\text{ethene}] + [\text{ethane}]}$$

The Cl# ranges from 4, indicating that only PCE is present and no dechlorination has yet taken place to 0, indicating that no chloroethenes are present (any more) and might have been dechlorinated.

In figure 11 the general characterisation scheme is summarised.

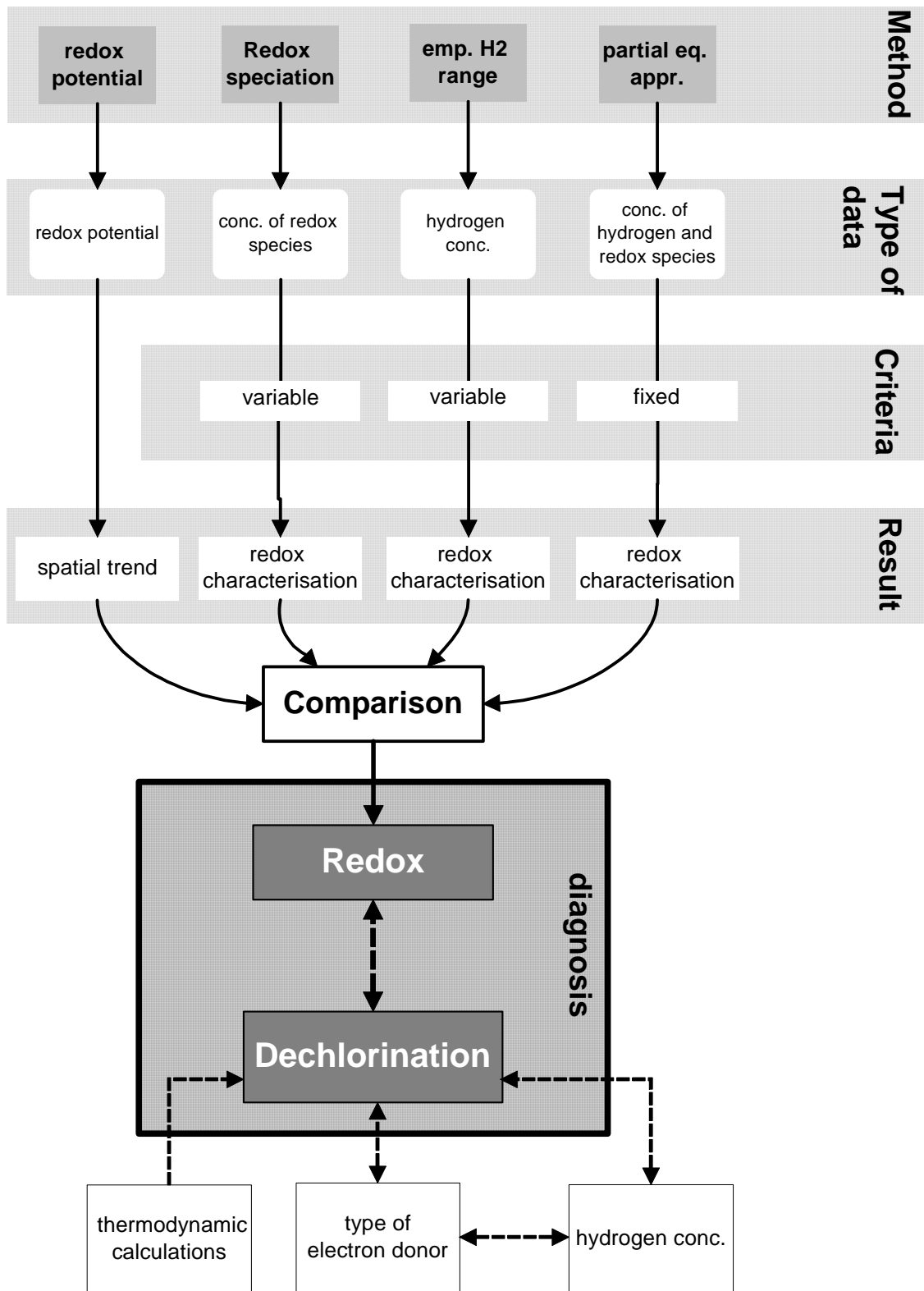
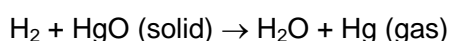


Fig. 11. General characterisation scheme showing the different steps that are taken to come to a diagnosis of redox conditions and dechlorination at the four case studies. Criteria that form the basis of the redox identification methods are either fixed, indicating that for all locations criteria are identical, or variable, indicating that they can be general for a particular type of location or have to be determined in a site-specific way.

MEASURING HYDROGEN IN THE FIELD**7.1 Introduction**

Hydrogen is a very small and reactive molecule, therefore it is necessary to measure hydrogen directly in the field. Transport of H₂-samples to the laboratory is not advisable. In the United States and Denmark a lot of experience has been obtained over the last five years with hydrogen measurements [Chapelle et al., 1997; Jakobsen et al., 1998]. Low concentrations of hydrogen can be measured with a gas chromatograph equipped with a reduction gas detector (RGD). This patented detector responds to reducing compounds that generate mercury from a mercuric oxide bed. The mercury vapour is detected by adsorption in the UV part of the spectrum.



The gas-stripping method is described by Chapelle as the best suited method for measuring hydrogen in the field [Chapelle et al., 1997]. Groundwater is pumped through a sampling bulb with a H₂-free nitrogen gas bubble. The dissolved hydrogen gas is being transferred from the water to the gas phase and asymptotically reaching equilibrium. The gas-stripping method is a kind of an accumulation technique. The H₂-concentration will increase from ppt levels in the water to ppb in the nitrogen bubble which can conveniently be detected by the reduction gas detector.

7.2 Operation procedure for hydrogen measurements in groundwater

Samples for hydrogen analysis were taken using the gas-stripping method developed by Chapelle [Chapelle et al., 1997]. Water from a well was continuously pumped through a 250 ml gas-sampling bulb with a flow of at least 500 ml/min. In some cases a flow rate of 360 ml/min was used. A 20 ml bubble of nitrogen gas was introduced into the sampling bulb through a septum. The slightly soluble hydrogen gas diffuses from the water to the gas phase. The equilibrium was achieved in about 25 minutes. Samples were taken after 25 and 30 minutes and when the difference was less than 5 %, it is assumed that equilibrium has been obtained.

A 2.5 ml sample from the gas bubble is taken with a gas-tight glass syringe and analysed immediately in the field using a gas chromatograph with a reduction gas detector from Trace Analytical (Bester, Amstelveen). The gas chromatograph is equipped with a Carbosieve II column and the loop size on the gas chromatograph is 1 ml. The carrier gas is N₂ with a flow rate of 20 ml/min. The column and detector temperature are 104 °C and 265 °C, respectively.

Hydrogen gas phase concentration values are converted directly into aqueous concentrations using Henry's law.



Fig. 12. Measuring hydrogen in the field, with the GC-RGD on a trolley.

7.3 Experimental section

7.3.1 Calibration

Calibration of the GC-RGD is carried out with three standard gases containing 1, 2 and 10 ppm H₂ in nitrogen. A 2.5 ml sample of the calibration gas was injected on to the gas chromatograph using a gas-tight glass syringe. Figure 13 shows a typical calibration curve.

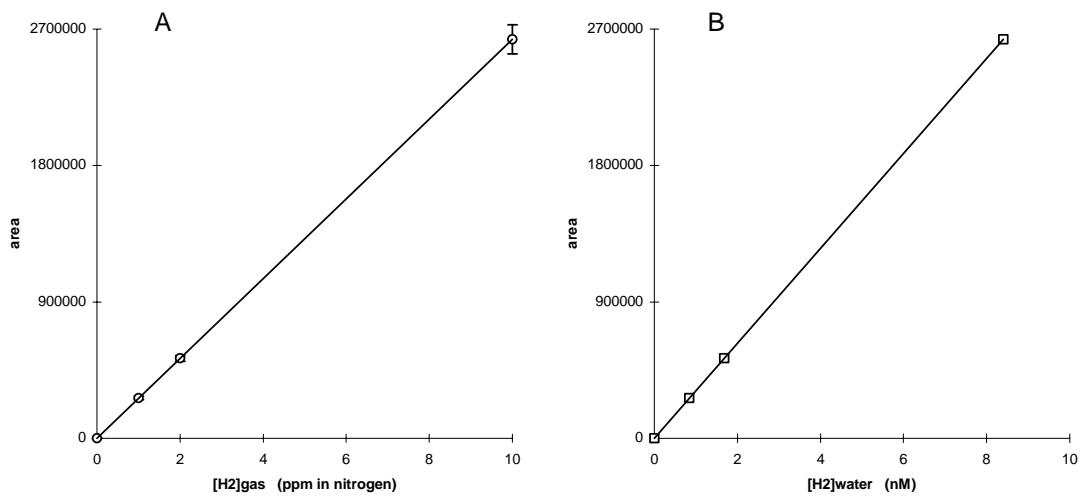


Fig. 13. Calibration of the RGD gas chromatograph. Graph A shows the results of the calibration measurements. Graph B shows the same results converted to the water phase. The results are the means of duplicate injections. $R^2 = 0.9999$.

7.3.2 Equilibrium

The developed method (groundwater sampling and analytical procedures) used in this study is similar to that described by Chapelle and Jakobsen [Chapelle et al., 1997; Jakobsen et al., 1998]. A test in the field was performed to check equilibrium times required and to get experienced with the method.

The first experiment is carried out using a groundwater sampling flow rate of 360 ml/min. Figure 14 shows two other equilibration control experiments.

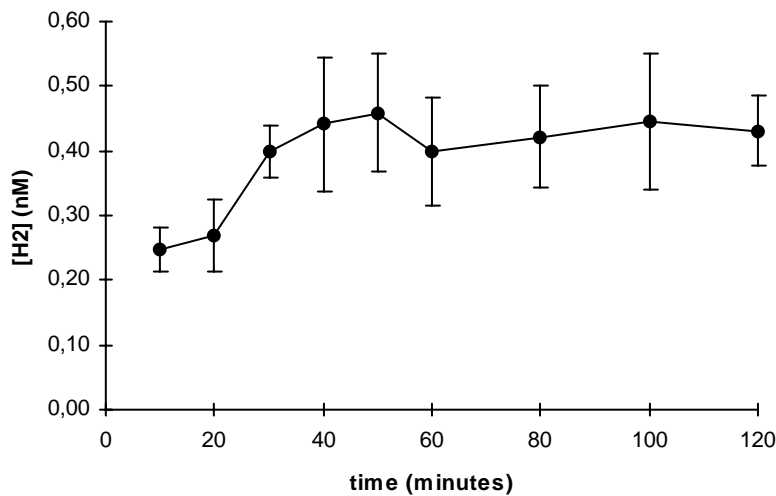


Fig. 14. Hydrogen concentration measured with the bubble-stripping method using a peristaltic pump. Flow rate: 360 ml/min. The results are the means of quadruplicate injections.

In about 30 minutes equilibrium was achieved, with a flow rate of 360 ml/min. In general in this study, a flow rate of 500 ml/min was used with corresponding equilibration times of 24 minutes. These results are consistent with the results of Chapelle and Jakobsen [Chapelle et al., 1997; Jakobsen et al., 1998]. They found that an increase of the flow rate from 500 to 1000 ml/min, equilibrium is achieved in proportionally less time (12 minutes).

Figure 15 shows two other equilibration control experiments.

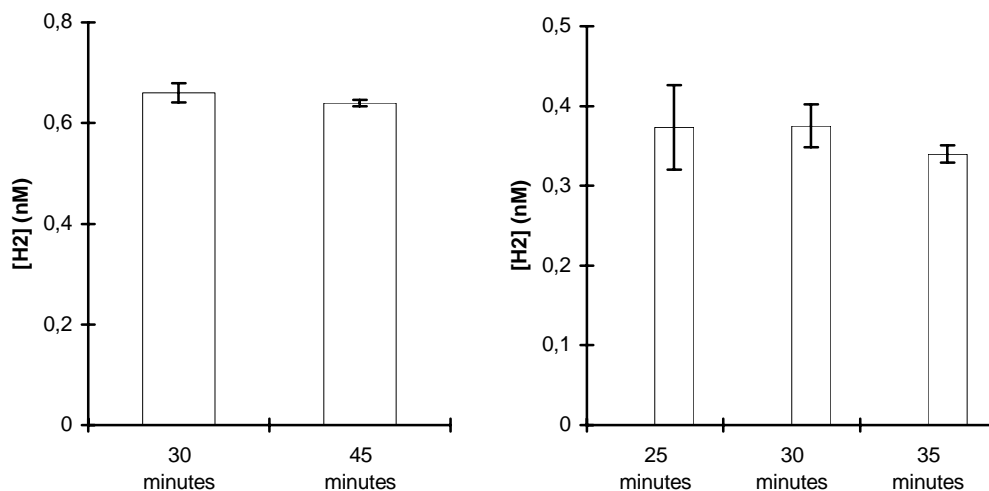


Fig. 15. Hydrogen concentration over time measured in two different wells with the bubble-stripping method using a peristaltic pump. Flow rate: 500 ml/min. The results are the means of quadruplicate injections.

In both experiments it appears that an equilibration time of 25 or 30 minutes is enough to obtain equilibrium. The difference between the first measurement and second or third one differs less than 5 %.

7.3.3 Type of pump

A comparison of different types of pumps was carried out by Chapelle [Chapelle et al., 1997]. Four methods for pumping groundwater were evaluated. These were a peristaltic pump, a stainless piston pump, a bladder pump and a stainless steel submersible pump. The submersible pump is not suitable because hydrogen can be produced through interaction between direct current and water. The three other pumps are suitable for pumping groundwater for hydrogen measurement.

In the experiments carried out in this study a peristaltic pump was used. In some experiments the bladder pump was used to compare results obtained with the peristaltic pump. A peristaltic pump, which draws water under a negative pressure, is not working properly when the water table is at a depth of more than five metres. A bladder pump, which pushes water under positive pressure upwards can be used at water table depths of more than five metres. A disadvantage of the bladder pump is the need to clean the pump before sampling a new well, which is laboriously and costly, to prevent cross contamination between different wells. In the Netherlands water tables deeper than five metres are not common and in most cases a peristaltic pump can be recommended.

Figure 16 describes two equilibrium curves, one is measured using the peristaltic pump and one is measured using the bladder pump. The sample was taken at a depth of 15 to 16 metre and the groundwater table was at a depth of 2.5 metre.

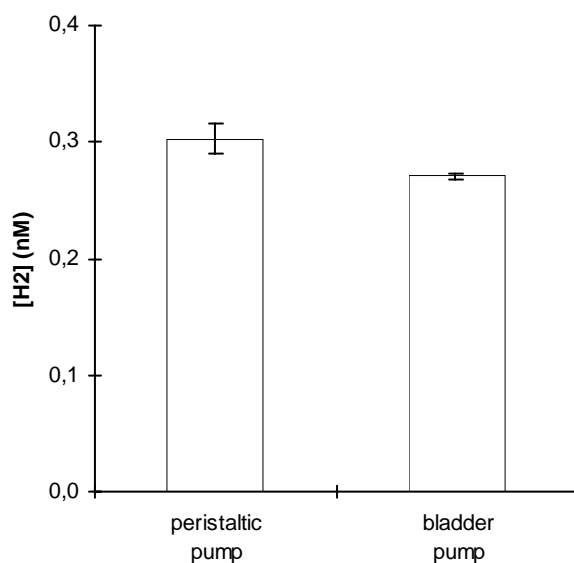


Fig. 16. Comparison of H_2 -concentrations sampled in the same well, during 30 minutes with a peristaltic pump (flow rate: 500 ml/min) and a bladder pump (flow rate: 680/ml/min). The results are the means of quadruplicate injections

The two pumping methods show similar results which is consistent with the findings of Chapelle. For measuring hydrogen in the field the use of a peristaltic pump is preferred since it has no risk of cross contamination. In some cases, if the water table is more than five metre, the bladder pump should be used. Special care must be taken of decontamination of the bladder pump and tubing material to avoid cross contamination.

7.3.4 Tubing material

Hydrogen is a very small molecule and therefore use of appropriate tubing material is required to minimise the transport of hydrogen through the tubing. According to the literature butyl rubber is

the most suitable tubing material. A disadvantage of this material is the high price, one metre costs about 2.50 Euro. It is recommended to use clean tubing material for each new well to avoid cross contamination, therefore butyl rubber is an expensive option. Figure 17 describes the comparison between butyl rubber tubing and the much cheaper tubing material polyethylene (PE). The price for 1 metre PE tubing is about 0.25 Euro.

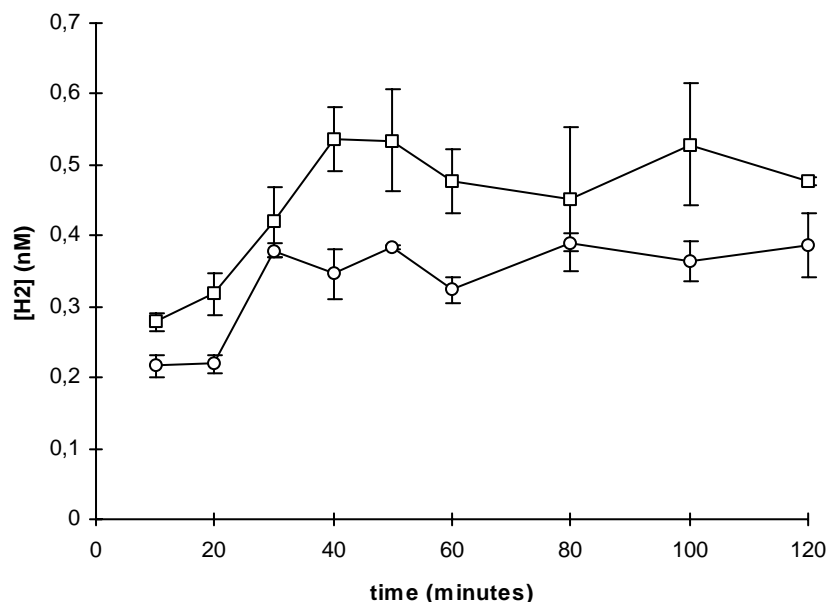


Fig. 17. Comparison of equilibration time of the gas-stripping procedure using butyl rubber tubing (○) and polyethylene tubing (□). Flow rate: 360 ml/min. The results are the means of duplicate injections.

The time required for equilibrium for both tubing materials is about 30 minutes. A small difference between the hydrogen concentration measured with the two different materials exists, with slightly higher H₂-concentrations for PE. Apparently PE tubing is a suitable material for hydrogen measurements.

7.4 Guideline for H₂-measurements in the field

General instruction

- Refresh the groundwater in the well with a volume equal to four times the volume of the well.
- Use clean PE tubing for each well.
- Clean the bladder pump (when used) carefully before sampling a new well to prevent cross contamination.

Instruction for H₂-measurements

- Use a pump with a flow rate of 500 ml/min:
 - use a peristaltic pump when the water table is less than 5 metre;
 - use a bladder pump when the water table is deeper than 5 metre.
- When the well has a discharge capacity too low to provide 500 ml/min, use lower flow rates and proportionally longer equilibrium times.
- Use a 250 ml gas bulb and connect this to the PE tubing and put on the pump:
 - fill the bulb with groundwater and remove the air in the gas bulb.
- Inject 20 ml of nitrogen in the gas bulb.
- Take four samples of the headspace for GC-RGD analysis with a glass gas-tight syringe.

- Take after 5 minutes (total time 30 minutes) again four samples and analyse. When the difference in hydrogen concentration is less than 5 %, it is assumed that equilibrium has been obtained.
- Inject several times a calibration gas with a hydrogen concentration between 1 and 10 ppm in nitrogen.
- To convert the hydrogen concentration in the gas phase to the concentration in the water phase the Henry coefficient is used. Figure 18 shows the Henry coefficient in relation to the temperature.

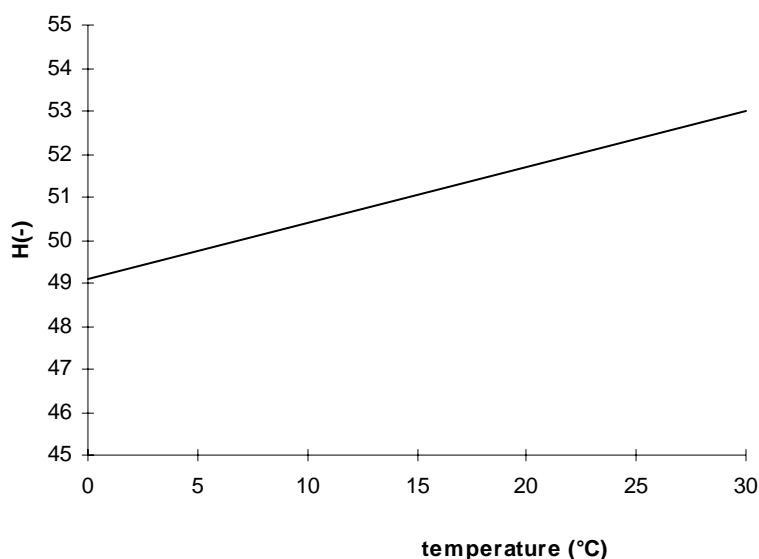


Fig. 18. The Henry coefficient in relation to the temperature [Lide and Frederikse, 1995].

Table 5 gives an overview of the main equipment needed for hydrogen measurements in the field.

Table 5. An overview of the main equipment.

gas chromatograph with RGD detector
N ₂ -carrier gas 10 litre 150 bar
pressure regulator (150 bar to 4 bar)
power supply (220 V, ± 350 W)
computer + interface
peristaltic pump (500 ml/min)
gas bulb (250 ml)
PE tubing
zero gas (H ₂ -free N ₂)
Cali-5 bond gas sampling bag with calibration gas (50, 10 and 5 ppm H ₂)
glass gas-tight syringe with luer lock and valve (2.5 ml)
plastic syringe (20 ml)

7.5 Costs of H₂-measurements

Besides reliability and practicability, the cost determine whether or not a particular measurement will be considered successful. Four different types of cost are taken into account:

- equipment costs;
- consumable costs;
- mobility costs;
- personal cost.

The cost of interpretation, data evaluation, and the assessment of the in situ redox conditions and dechlorination is not incorporated. The cost is purely based on the measurements of hydrogen concentrations in groundwater. The costs mentioned in the rest of the text are mentioned without value added tax (VAT).

Equipment costs involve solely the fixed costs of the portable gas chromatograph, while consumable costs include all recurring costs such as: maintenance of the GC, tubings and reagents. Mobility costs are made to reach the site and include the vehicle and fuel. The personal costs include the rates of two engineers that have to drive to the site and to do the measurements.

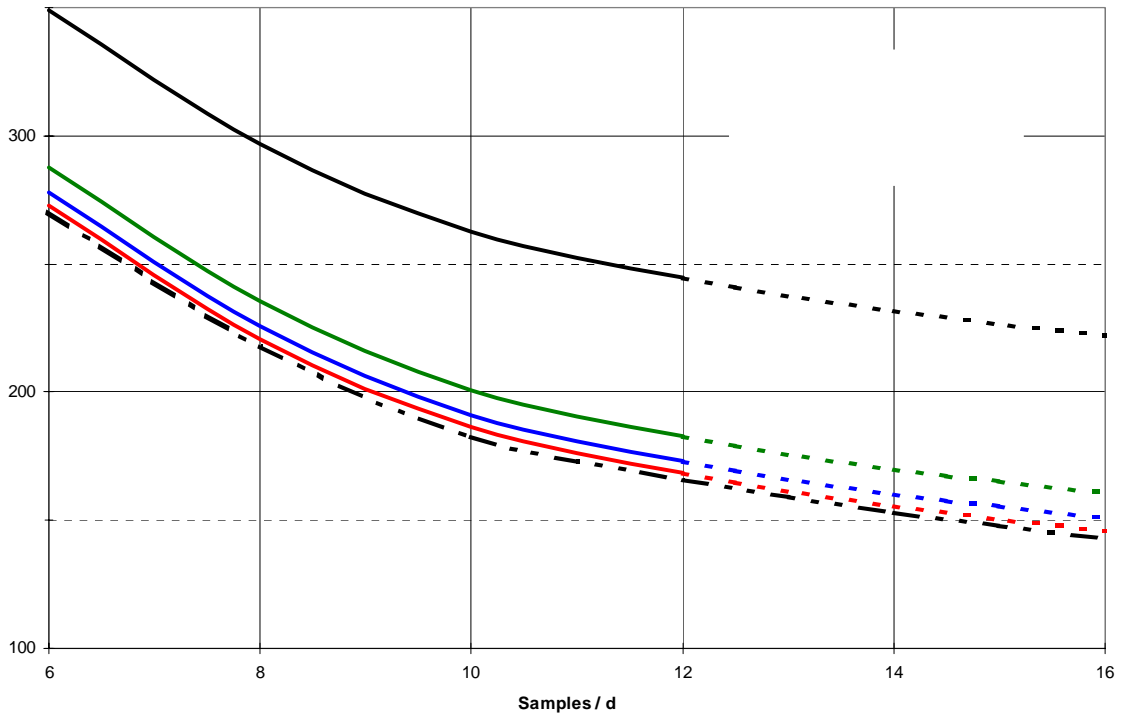
In order to properly estimate the costs of a the hydrogen measurement the following aspects have to be considered:

- number of samples taken (per day and per year);
- measurements of other species;
- distance travelled;
- working hours per day.

The costs are estimated for a typical hydrogen analysis. Since these costs strongly depend on the aspects mentioned above, the cost dependency is shown in two different figures. In the first one, the hydrogen measurement costs are shown to be dependent on both the amount of samples taken per day and the amount of samples that are taken per year. The costs decrease with the amount of samples taken per year and per day, but not linearly. For a relatively small amount of samples taken per day costs decrease very sharply, but after about 10 to 12 samples per day (the number of samples that can be taken during one working day) the costs do not decrease substantially when increasing the amount of samples per day. The same applies to the amount of samples per year. Initially, for a relatively small amount of samples per year, the costs change significantly, but above 400 S/y the cost do not decrease drastically (see fig. 19).

In figure 20 the specification of the costs is shown assuming that ten samples are taken per day and 200 per year. The personal cost for the engineers forms the major part of the total costs (41 %). The equipment cost form 31 % of the total costs. Mobility costs strongly depend on the situation of the location but only form a small part of the total costs (6 %). Costs for consumables is estimated to form 22 % of the total costs.

Cost of Hydrogen Analysis Depending on Amount of Samples



RADEMARKT LOCATION

8.1 Description of the Rademarkt location

The Rademarkt location is situated in the centre of the city Groningen (the Netherlands). From 1969 to 1990 a chemical laundry was situated in a former building at Rademarkt 25. Due to spillage to the sewer system chloroethenes have been transported and contaminated the soil and groundwater. In the direction of the groundwater flow a contaminant plume has developed. Additionally, the same site was polluted with BTEX by a garage which was established at Rademarkt 25 from 1955 to 1969. Both plumes partly overlap as is shown in figure 21.

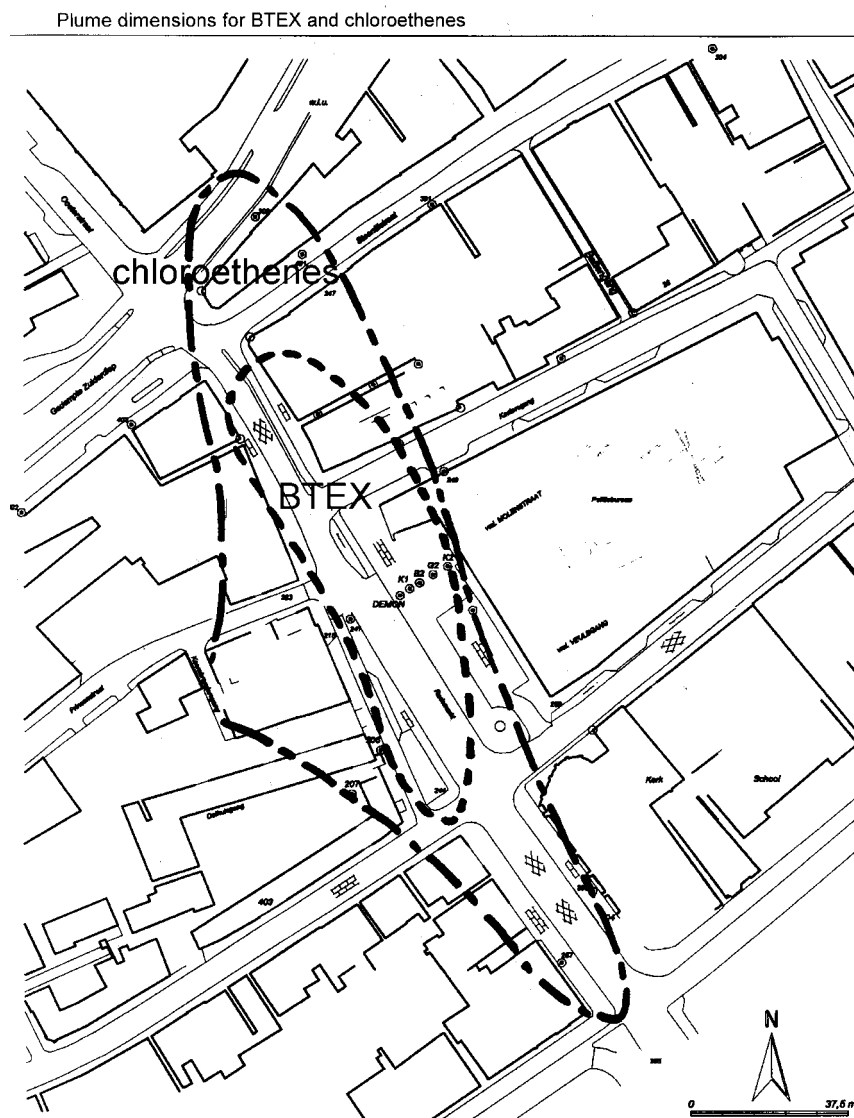


Fig. 21. Rough schematic representation of the dimensions of the chloroethene and BTEX plume at the Rademarkt site. Contours are based on previous measurements and represent concentrations above $1 \mu\text{g/l}$.

The contaminants are primarily present in a sandy loam top layer of 8 metres thick. At a depth of 8 metres to 12 metres a loam layer is present below which a sandy aquifer is located. The

phreatic groundwater flow is slow and in a variable direction ranging from northeast to south-east. The groundwater flow in the first aquifer is directed mainly to the east.

The Rademarkt site has been studied in various projects. In a former NOBIS project [CUR/NOBIS, 1997] the redox conditions have been identified. It appears that stronger reduced redox conditions are found in the highest contaminated zones. The correspondence between low redox conditions and the source zone of the plume has been explained by the presence of BTEX compounds and DOC leaking from the sewer. These compounds act as electron donors that reduce electron acceptors, and cause a decrease in redox conditions. At the edges of the plume, such influence is not present and the redox conditions approach the natural background, i.e. oxygen-, nitrate- or iron-reducing. These sequential redox conditions between the different redox zones favour the degradation process of the chloroethenes since the higher chlorinated ethenes dechlorinate under strongly reduced conditions in the core of the plume, and the lower chlorinated ethenes can be oxidatively degraded under less reduced conditions in the periphery of the plume.

8.2 Redox characterisation

In a previous project redox conditions have been identified at the Rademarkt location [CUR/NOBIS, 1997]. This characterisation has been done on basis of macro chemical analysis of the following species in groundwater: oxygen, nitrate, nitrite, total iron, divalent iron, sulphate, sulphides and bicarbonate. By doing so, a rough interpretation could be made in which transitional redox zones could be indicated but not defined in detail. In the additional characterisation reported here the redox conditions are more thoroughly identified by using several different methods: the traditional methods involving redox potential measurements (Eh) and macro-chemistry (see fig. 22 and 23). Hydrogen measurements will be interpreted in two different ways; by comparing measured hydrogen concentrations to an empirically determined range and by the partial equilibrium approach (see fig. 24 and 25). In the following paragraphs the exact criteria for the different approaches are formulated and applied to the Rademarkt location.

Sampling points distributed over the highly contaminated parts of the plume and in the periphery of the plume were selected. All the wells had a filter depth between 4 to 9 metres. For each redox identification method, redox conditions are indicated on a map of the location.

8.2.1 Redox potential

The redox potential could not be used directly to identify redox conditions. However, the redox potential might be used to observe spatial redox trends, in which zones can be distinguished as either more or less reduced, without identifying the actual redox condition. In further chapters the results of the redox potential are compared to the results of the other methods.

In figure 22 the redox potential is shown for several wells. The pattern does not display a clear and logical trend, since a large variation has been found on relatively small scale. It is therefore not considered to be a basis for an interpretation of the redox situation at this site.

8.2.2 Macrochemistry

For the Rademarkt location the criteria for a typical location (see chapter 6) can be used as a basis for the macro chemical method (see fig. 26).

CH ₄ > 1 mg/l	→yes: methanogenic
↓	
SO ₄ < 1.5 mg/l	→yes: sulphate-reducing
Fe(II) > 1.5 mg/l	
↓	
O ₂ > 1 mg/l	→yes: oxygen-reducing
↓	
NO ₃ > 0.5 mg/l	→yes: nitrate-reducing
↓	
no:	iron-reducing

Fig. 26. Criteria for the macro chemical method.

These criteria have been used to characterise the redox conditions at several different sampling points. High methane concentrations, which form the criteria for methanogenesis, are found at two sampling points (404 and 304). Sulphate-reducing conditions, indicated by decreased sulphate concentrations in combination with increased iron concentrations, are found only at sampling point 247. Oxygen is below 1 mg/l throughout the site, except for one sample (305). Nitrate concentrations seem to be strongly related to divalent iron concentrations. For samples where nitrate concentrations were below the detection limit, the divalent iron concentrations were higher than the detection limit, and vice versa (except for sample 401 where both nitrate and divalent iron occur simultaneously). Increased nitrate concentrations indicate nitrate-reducing conditions at the following sampling points: G2, 244, 403, 401, 303, 215 and 223. At three sampling points iron-reducing conditions take place: DEMO, B2 and 259.

So, redox conditions have been found to vary from oxygen-reducing to methanogenic (see fig. 23). The most reduced conditions (sulphate-reducing and methanogenic) occur in a zone which is following the dimensions of the contaminated plume. However, possibly due to the influx of nitrate rich groundwater this strongly reduced zone is more narrow than would be expected on basis of the plume dimensions. Nevertheless, the redox conditions seems to be related to the contaminated plume since nitrate-reducing redox conditions dominate outside the plume. At sampling point 304 methanogenic conditions have been identified, although it is not located in the core of the plume.

8.2.3 Comparing hydrogen concentrations with empirically determined hydrogen ranges

Hydrogen concentrations have been measured at several sampling points throughout the Rademarkt location (see table 6).

Table 6. Measured hydrogen concentrations in nM.

sampling point	[H ₂] in nM	sampling point	[H ₂] in nM
demo	0.36	304	0.17
B2	0.29	401	0.12
G2	0.18	247	7.29
259	0.49	303	0.09
404	0.37	215	0.14
244	0.17	305	-
403	0.11	223	-

The steady-state hydrogen concentrations that are associated with redox processes are temperature dependent. Therefore, measured hydrogen concentrations must be compared to empirical determined ranges for the local temperature. At the Rademarkt location the temperature ranges between 10 °C and 15 °C and the typical empirical hydrogen range for Dutch situations can be used (see table 7 and table 4 section 4.2.1).

Table 7. Criteria for the empirical hydrogen ranges for typical Dutch situations.

hydrogen concentration		redox condition
$H_2 < 0.2$	→	nitrate-reducing
$0.2 < H_2 < 0.3$	→	iron-reducing
$0.3 < H_2 < 1.5$	→	sulphate-reducing
$H_2 > 1.5$	→	methanogenic

These criteria have been used for the redox identification as depicted in figure 24. Redox zones similar to the macro chemical method have been identified with this method. The distribution of zones with sulphate-reducing and methanogenic redox conditions seems to be related to the presence of the contaminated plume, although there is not a perfect fit. Nitrate-reducing conditions do not only exist outside the plume, but also enter the plume from the western and eastern side. Therefore the strongly reduced zone appears to be relatively narrow.

In some parts there is a transitional zone in which redox conditions change from more to less reduced. This redox transition at some parts occurs very abruptly, i.e. from methanogenic to nitrate-reducing on a very short distance. In other parts a more gradual transition is observed, where the conditions change from sulphate-reducing to iron-reducing and then to nitrate-reducing, over large distances.

8.2.4 *Partial equilibrium approach*

Based on the many parameters that have been measured for several different reactions, Gibbs energies can be calculated. Some reactions have not been covered for several reasons. Manganese reduction has not been covered since manganese (hydr)oxides are generally not present in high amounts in Dutch soils to be an important electron acceptor. Sulphides have not been measured because they were assumed to precipitate to iron sulphides as soon as they were produced. Therefore the reaction from sulphate to sulphide has not been included. Instead, a reaction is covered in which sulphate reacts directly to iron sulphide. For the nitrate-reducing reaction only the one in which nitrate reduces to nitrogen has been taken into account. The nitrogen concentration has not been measured but assumed to be at maximum solubility ($5.15 \cdot 10^{-4}$ M). Nitrite and ammonium have not been measured and the reactions in which nitrate reduces to these products have not been taken into account. Concentrations from species which were below the detection limit and concentrations which were unreliable when low (e.g. oxygen below 1 mg/l) were discarded and consequently the involving reaction was assumed not to take place. For the iron-reducing reaction goethite has been selected to be the predominant iron(III) mineral.

For relevant reactions, Gibbs energies have been calculated. Based on this energy, reactions have been determined as being favourable if Gibbs energies are more negative than threshold, or as unfavourable if it exceeds the threshold. For reasons discussed in chapter 6, the value of the threshold has been chosen to be -5-kJ/mol. From the Gibbs energies that have been calculated for many reactions at this site, it appears that Gibbs energy values are clustered slightly below -5 kJ/mol. This clustering implies that these values might indicate the actual threshold Gibbs energy, since bacteria tend to operate at situations as close as possible to this threshold.

For several sampling points the redox conditions have been identified by using the partial equilibrium approach (see fig. 25). Also these results show that more reduced conditions correspond to the source zone of the contaminated plume. Outside the plume nitrate-reducing conditions dominate, at the edges intermediate conditions exist and inside the plume more reduced conditions. In the western and eastern part of the plume nitrate-reducing conditions take place, narrowing the zone of highly reduced conditions.

Some regions can be considered as transition zones in which more redox reactions occur simultaneously. Very clearly, a gradual change in redox conditions can be observed in these zones. In the northern part of the location conditions change from methanogenic/sulphate-reducing inside the plume to sulphate/nitrate-reducing conditions and nitrate-reducing conditions outside the plume. Furthermore in the centre of the plume redox conditions change from iron/sulphate-reducing to nitrate-reducing.

8.2.5 *Comparison of the methods*

Except for the redox potential the different methods all give results that are consistent with each other. It appeared that a sulphate-reducing and methanogenic zone exist in the vicinity of the contaminated plume. A complete fit has not been found since nitrate-reducing conditions from outside the plume appear to penetrate the plume on both the western and eastern side.

Only small differences exist between the three different methods, especially the distinction between nitrate and more reduced conditions could be made perfectly in each method. Only small differences between the methods have been found for iron-reducing, sulphate-reducing and methanogenic conditions, but a relatively large difference has been found at sampling point 304 where according to the macro chemical method methanogenic and according to the empirical hydrogen method nitrate-reducing conditions exist. Unfortunately, the partial equilibrium approach could not give a decisive answer at this point due to a lack of macro chemical data.

The partial equilibrium approach has been shown to be a useful method because it was able to account for the discrepancy between the two other methods. At samples for which the macro chemical and empirical hydrogen method indicated distinct dominant redox processes, the partial equilibrium approach often appeared to cover the redox processes according to both other methods. These sample locations are often found in a redox transition zone, an area where more redox processes are likely to take place simultaneously. The partial equilibrium approach identified simultaneous favourable conditions for various redox processes, i.e. iron- and sulphate-reducing conditions and simultaneous sulphate-reducing and methanogenic conditions, and even simultaneous nitrate-reducing and sulphate-reducing conditions. All these combined redox processes were identified in redox transition zones and were consistent with the rest of the redox pattern.

8.2.6 *Conclusion for redox characterisation*

Thus, the partial equilibrium approach has been shown to give very the most detailed and consistent redox interpretation at this location, since it is capable to identify zones where different redox processes simultaneously can occur (redox transition zones). However this method requires an extensive set of measurements including both redox parameters and hydrogen measurements. The macro chemical method and the empirical hydrogen range, which are less extensive, can be used to get an indication of the redox processes, but are incapable to indicate the transition zones. The redox potential has not been found to match with any of the other methods and seems to be an inappropriate tool for redox characterisation of this site. Measuring hydrogen has proved to be beneficial since it provides a stronger based redox characterisation than by macro chemical methods alone.

8.3 Hydrogen and dechlorination

The ultimate goal is to find a tool to quantify and control dechlorination processes. In this section the usefulness of hydrogen is tested by finding relations with dechlorination. These relationships could be either direct, when hydrogen concentrations are directly coupled to dechlorination processes, or indirect, when relationships exist between redox identification methods based on hydrogen and dechlorination. Also relationships between hydrogen concentrations and different carbon sources are being investigated.

Similar to other sites, also at the Rademarkt site dechlorination reactions with hydrogen as electron donor have been found to be energetically highly favourable throughout. Gibbs energies could not be calculated for all dechlorination reactions, the ones that have been calculated were all in a range between -122 kJ/mol and -158 kJ/mol (see table 8), well below the threshold for ATP-synthesis. Thus from a thermodynamic point of view dechlorination should not be hindered in any part of the site. The lowest Gibbs energies have been found for PCE dechlorination to TCE, showing to be a very favourable dechlorination reaction. The highest Gibbs energies have been found for the less, but still highly favourable reactions of the lower chlorinated ethenes. Furthermore, the hydrogen concentrations are positively coupled to the energetics of the reaction. The lowest Gibbs energies are calculated at points where high hydrogen concentrations are present, and these points have been determined to be the most reduced (see section 8.2).

Table 8. Calculated Gibbs energies (in kJ/mol) of dechlorination reactions with hydrogen.

	PCE dechl.	TCE dechl.	DCE dechl.	VC dechl.	ethene reduction
pb demo	-148	-141	-125	*	*
pb B2	-148	-140	-125	*	*
<i>pb G2</i>	<i>-152</i>	<i>-140</i>	<i>-127</i>	*	*
pb 259	-152	*	*	*	*
pb 404	-153	*	*	*	-63
pb 244	-154	-142	-124	-122	-69
pb 403	-148	-137	*	*	*
<i>pb 304</i>	<i>-148</i>	*	*	*	*
pb 401	-146	-137	*	*	*
pb 247	-157	*	*	*	-77
pb 303	-145	-134	*	*	*
pb 215	-149	-140	-126	-128	-61

* the required chloroethenes for this reaction have not been detected

italics pH has been extrapolated

Thus thermodynamics indicate that dechlorination is more favourable at zones where high hydrogen concentrations exist, but the actual relationship between hydrogen and dechlorination has not been proven. The dechlorination stage of the Rademarkt can be quantified by the chloride number (Cl#, see chapter 6).

The redox characterisation that has been made shows that the most reduced conditions exist in the core of the contaminated plume. Those conditions are sulphate-reducing and methanogenic and are thus considered to be favourable for dechlorination processes. In these zones the Cl# is expected to be low, since the lower chlorinated ethenes will be present in relatively high concentrations. In the periphery of the plume where nitrate-reducing conditions exist, reductive dechlorination will not play an important role and high concentrations of higher chlorinated ethenes will

result in high chloride numbers. A strong correlation between dechlorination and redox conditions, however, has not been observed at the Rademarkt site (see fig. 27). The bulk of the samples have Cl# between 2 and 4. At two points, however, Cl# numbers are significantly lower than that. At sampling point 247 low Cl# suggest that dechlorination is in far stage, which could be in accordance with the redox conditions that are determined as methanogenic. Unfortunately, at sampling point 304 where also a lowered Cl# has been observed no relation could be made between the dechlorination process and redox conditions, since no consistent redox characterisation could be made. According to the empirical hydrogen method the conditions are nitrate-reducing, while the macro chemical method indicated methanogenic conditions.

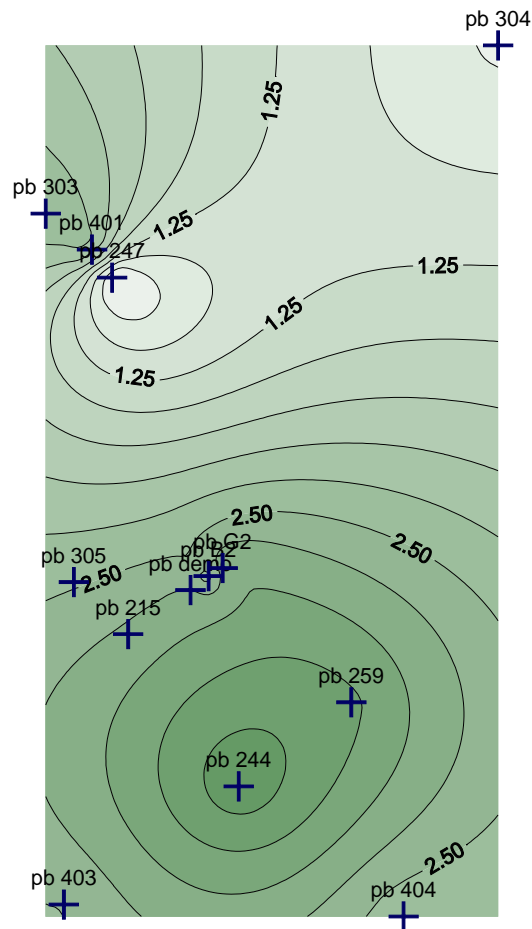


Fig. 27. Contour plot of Cl#, based on Kriging method.

A direct correlation between dechlorination and hydrogen concentrations has not been found. In figure 28 the hydrogen concentration is plotted against the Cl#. The points with the lowered Cl# correspond to the same points that have been discussed above.

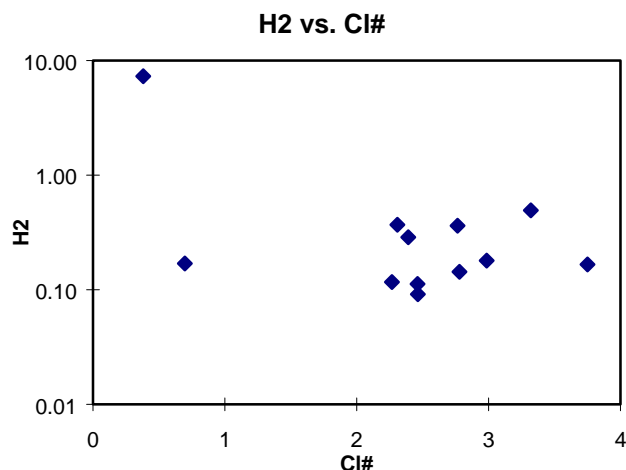


Fig. 28. Plot of hydrogen against chloride number.

Although no clear correlations have been found between hydrogen and dechlorination, hydrogen appears to be related to the DOC content in the groundwater (see fig. 29). It seems that high DOC contents cause high hydrogen concentrations. DOC is the sum of all carbon compounds that are dissolved in the groundwater including many compounds that could be fermented to hydrogen.

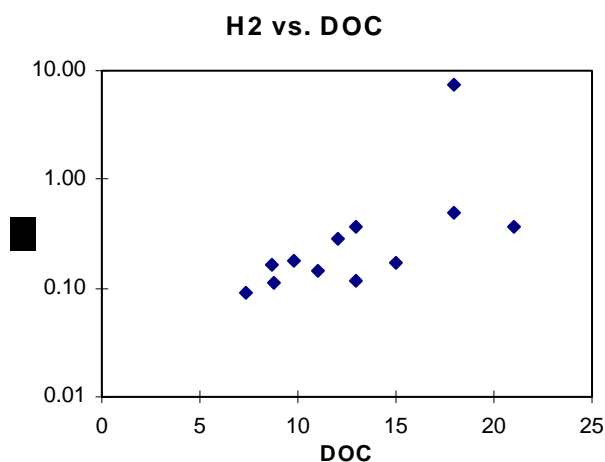


Fig. 29. Plot of hydrogen against DOC.

8.3.1 Conclusion of hydrogen and dechlorination

Although from a thermodynamic point of view dechlorination is considered more favourable at high hydrogen concentrations, a proof that an enhancement of dechlorination processes takes place at high hydrogen levels has not been found for the 'natural' situation at the Rademarkt location. But, for the point with the lowest Cl# the highest hydrogen concentration and methanogenic conditions have been determined, suggesting that there is a relation between hydrogen concentrations and redox conditions on one hand and dechlorination on the other.

Data analysis showed a significant correlation between DOC (a potential electron donor for dechlorination) and hydrogen. More research is needed to support these observations.

CHAPTER 9

DAF LOCATION

9.1 Description of the DAF location

9.1.1 *Situation*

The location is about 17 acres (7 hectare) and forms a part of the DAF industrial terrain which is about 220 acres (90 hectare). In the central part of the location DAF started its activities in 1949. This part has been used and is still being used for production and maintenance activities and is considered the most contaminated part of the entire terrain. The main source of this contamination is located on the northwestern side of the building, where until 1975 metals have been cleaned and chemicals have been stored.

9.1.2 *(Geo)hydrology*

The surface layer of the DAF location forms a part of the Nuenen formation. Locally this formation consists of a sequence of loamy sand and loam. Additionally, in the upper seven meters of the profile thin peat layers are present. The Nuenen formation reaches to 25 - 30 metres depth. Below this layer there is an aquifer consisting of coarse sand and gravel.

The average groundwater level is at 2.5 metres below ground level. The direction of the groundwater flow is variable with depth:

- on 3 - 4 metre depth the groundwater is south to southwesterly directed. On the western part of the location the groundwater turns off to the west;
- from 6 - 8 metre depth the groundwater is directed to the southwest;
- around 14 - 15 metre depth, the groundwater is directed northwesterly. Also the water in the aquifer is flowing in this direction.

9.1.3 *Description of the contamination*

The DAF location has been contaminated with both volatile aromatics and chlorinated solvents. The source of both contaminants is located northwest of building E55 around well C40. In the direction of the groundwater flow a plume has been developed. In preliminary investigations TRI has been found to be the major contaminant. However, in more recent research the contamination consisted mainly of CIS and VC, indicating that dechlorination has taken place. Also a limited ground contamination has been found for TRI and is closely coupled to the presence of the groundwater contamination. Additional contaminated sources have been identified at two spots. Around C40 a BTEX contamination partly overlaps the chloroethene plume and around C46 a DCA source has been located.

9.1.4 *Arrangement of the wells*

Around twenty wells throughout the site have been selected and sampled for all relevant parameters that are needed to characterise redox conditions by four different methods, and to analyse dechlorination processes. Most wells have been sampled at different depths. Two approaches have been followed in this chapter. For the first approach layers have been selected at three different depths, at 6 - 8 m, 15 - 28 m,

Fig. 30. Site map including the selected flow path. The flow path curve is a result of infiltrating canal water into the upper 'Nueneen' formation. The regional groundwater flow direction in the underlying aquifer is in the direction from NOB2 to NOB3.

9.2 Redox characterisation

In order to understand the biodegradation process of chloroethenes at the DAF location it is important to identify the redox conditions that exist. Four different methods will be used and tested for their applicability to identify the redox conditions. The results will be presented in two different ways, one in three layers of depth and the other in a depth profile along the groundwater flow.

9.2.1 Redox potential

Similar to the locations which have been described in other chapters, the redox potential has only been used to identify trends in redox conditions on this location. A statement of the exact redox condition that exists is not considered to be reliable (see chapter 4).

In contrast to the other redox identification methods, the redox potential is only presented in a depth profile and not in layers. In figure 31 is shown that the redox potentials range between -31 mV and -260 mV. Roughly, three zones with different redox potentials could be distinguished in the chloroethene/BTEX plume. In the source a redox potential of -100 to -200 mV has been found. Even lower redox potentials of -200 to -250 mV are present in a zone halfway downstream the plume. In the deepest parts far away from the source, redox potentials are higher again and range from -50 to -100 mV. Outside the chloroethene plume a less consistent pattern was present. Low redox potentials are found in the vicinity of the canal, and higher values for most other parts. Also relatively high redox potentials have been found for the zone associated with the DCA contamination, which is not in accordance to expectations since these contaminants can act as electron donor and consequently cause a drop in redox conditions.

Fig. 31. Soil profile with redox potentials.

9.2.2 *Macrochemistry*

On basis of the macro chemical criteria formulated for typical locations (chapter 6), redox conditions could not be defined properly. Probably the background concentrations and the processes that take place at the DAF location are very distinct from the typical situation for which the redox identification protocol was developed. This resulted in an ambiguous redox interpretation in which methanogenic conditions are identified for samples where divalent iron is not even increased, and sulphate-reducing conditions could not be identified at all, since the sulphate concentrations were higher than the criteria at all sampling points probably due to increased background concentrations. It is unlikely that methanogenic conditions take place together with iron-reducing conditions, without the occurrence of sulphate-reducing conditions is not very likely. Therefore the standard protocol appears to be inappropriate and macro chemical criteria have to be formulated site-specifically, in order to be able to identify the redox conditions at the DAF site (see table 9).

The presence of oxygen and nitrate is indicative for oxygen- and nitrate-reducing conditions. Although at the DAF location oxygen has been encountered in the groundwater in considerable concentrations, the measurements are not considered to be reliable. It is suspected that the sampling method or an erroneous oxygen detection caused these strange results. Nitrate which is commonly present under oxygen-reducing conditions, is in fact absent throughout the site. Redox conditions are therefore considered to be more reduced. Iron-reducing, sulphate-reducing and methanogenic conditions seem to play an important role. Manganese-reducing conditions, on the other hand, are not expected to be important, because in the Dutch subsurface manganese (hydr)oxides are only present in small amounts.

Iron-reducing conditions can be demonstrated by the loss of trivalent iron and the production of divalent iron. Trivalent iron is always present as mineral phase and has not been measured. Divalent iron is dissolved in the groundwater and has been measured thoroughly. Increased concentrations of divalent iron might indicate that iron reduction has taken place, but it could also have been transported from elsewhere. The absence of divalent iron might indicate that iron

reduction has not (yet) taken place. In this case it is also possible that iron reduction has taken place but the produced divalent iron directly precipitated as iron carbonate or iron sulphide. This could explain that certain samples at the DAF location did not contain divalent iron, although both oxygen and nitrate were absent. As criterion for the characterisation of iron-reducing conditions therefore not the presence of divalent iron but the absence of oxygen and nitrate will be used.

Sulphate reduction can be demonstrated by the disappearance of sulphate and the production of sulphides. In this project only sulphate has been selected, since sulphide concentrations are disturbed by the precipitations with divalent iron to form iron sulphides. Decreased sulphate concentrations suggest that sulphate reduction has taken place. However, sulphate concentrations are not always reliable as redox parameter since sulphate might have been transported from elsewhere. A difficulty which is encountered in this method is the distinction which must be made between high and low sulphate concentrations. For the DAF location values of 10 mg/l and 20 mg/l have been selected as criteria. The selection of these values is based on the (statistical) distribution of sulphate concentrations. The group with sulphate concentrations below 10 mg/l is considered as sulphate-reducing (or methanogenic). Another group could be identified above a value of 20 mg/l. In this group the high sulphate concentrations indicate that sulphate reduction has not taken place and iron reduction is more likely. For the group between the two values it is uncertain if sulphate has been reduced, and therefore both processes possibly take place.

During methanogenesis bicarbonate is being reduced to methane. Especially methane might be a good indicator for the occurrence of methanogenesis. However its use is limited if methane is being transported from elsewhere or if methane is locally produced by processes other than methanogenesis (e.g. dechlorination of chloromethanes). Also for methane the distinction between high and low concentrations forms an obstacle. Based on the distribution of the data, two groups have been identified. The group having methane concentrations above 5 mg/l is identified as methanogenic, provided that sulphate concentrations were below 10 mg/l and oxygen and nitrate were absent. The other group has methane concentrations below 5 mg/l and is considered as sulphate-reducing.

Table 9. Overview of the site-specific criteria on which the redox conditions have been identified following the macro chemical method.

redox characterisation	criteria		
iron-reducing	O ₂ + NO ₃ absent	SO ₄ ²⁻ > 20 mg/l	
iron/sulphate-reducing	O ₂ + NO ₃ absent	10 < SO ₄ ²⁻ < 20 mg/l	
sulphate-reducing	O ₂ + NO ₃ absent	SO ₄ ²⁻ < 10 mg/l	
methanogenic	O ₂ + NO ₃ absent	SO ₄ ²⁻ < 10 mg/l	CH ₄ > 5 mg/l

In figure 32 the redox conditions are shown at three different layers. In the upper layer in most parts the redox conditions have been identified as iron-reducing. At two other parts a combination of iron- and sulphate-reducing conditions exist. Those parts are found at the eastern part of the location. The same pattern could be found in the second layer except that the more reduced area has been moved in a northern and western direction. In the deepest layer a more heterogeneous pattern is shown. Sulphate- and iron-reducing conditions alternate at a small scale.

From the profile (see fig. 33) it does not become clear that the redox conditions are associated with the contaminated plume.

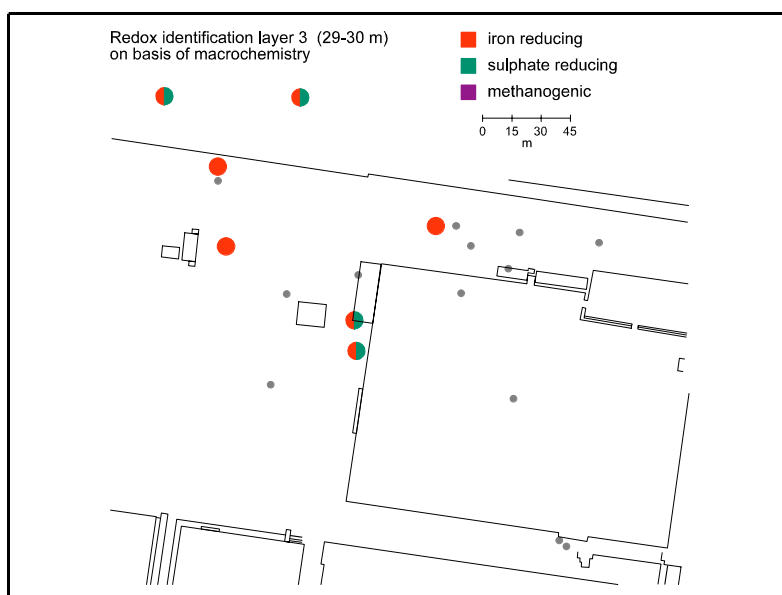
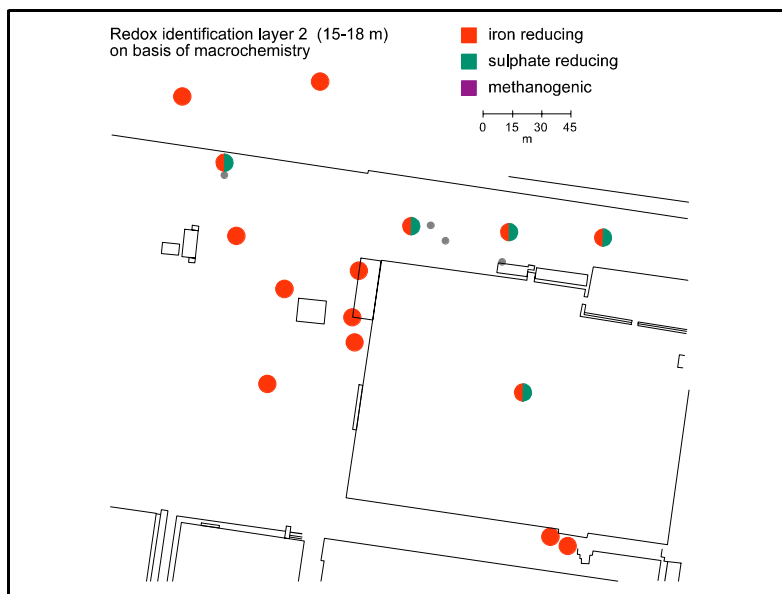
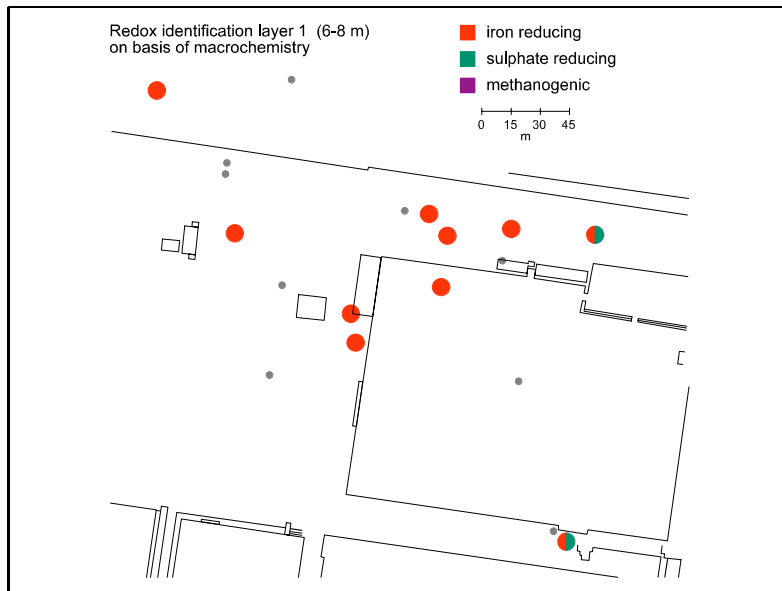


Fig. 32. Redox characterisation in layers according to macro chemical method.

Fig. 33. Redox characterisation in the depth profile according to the partial equilibrium approach.

9.2.3 Comparing hydrogen concentrations with empirically determined hydrogen ranges

The following hydrogen concentrations have been measured at the DAF location (see table 10)

Table 10. Hydrogen analysis.

sampling point	[H ₂] in nM	sampling point	[H ₂] in nM
NOB5-1	0.46	C39-2	0.23
C4-2	0.23	C41-1	0.11
C40-1	4.77	NOB4-2	0.53
C40-2	1.09	C4-3	0.63
C47-2	0.49	C32-2	0.25
NOB2-1	3.07	C48-3	0.44
NOB3-1	0.30	B12	0.13
C33-1	0.20	C51-3	1.01
NOB1-1	0.80	C47-4	0.54
C32-1	0.18	NOB2-3	1.15
B12	0.40	NOB3-3	2.49
C47-3	0.50	C27-3	0.27
C46-2	0.29	NOB1-3	0.40
NOB2-2	4.92	C41-2	0.25
NOB3-2	0.29	C48-4	4.25
C45-3	0.46	NOB4-3	0.66
C27-2	0.13	C61	1.30
C33-2	0.10	C61	0.58

At the low temperatures of about 14 °C that exist at the DAF location, the empirical hydrogen range which is based on results of experiments at standard temperature, could not be used. Instead, the empirical range for temperatures between 10 °C and 15 °C is also applied to the DAF location (see table 11 and table 4 section 4.2.1).

Table 11. Criteria for the empirical hydrogen method.

hydrogen concentration		redox condition
$0.2 < H_2 < 0.3$	→	iron-reducing
$0.3 < H_2 < 1.5$	→	sulphate-reducing
$H_2 > 1.5$	→	methanogenic

For each layer of depth the hydrogen concentrations have been compared to the empirical range in order to determine the redox conditions (see fig. 34). According to this method a combination of iron-reducing, sulphate-reducing and methanogenic conditions is found in all layers. On a relatively small scale, the redox conditions show a large variation.

In the upper layer two spots have been identified as methanogenic, four as sulphate-reducing and three as iron-reducing. These spots appear to be randomly distributed, however in the second layer the same spots have been found to be in a highly reduced stage. At this depth it becomes more clear that the sulphate reduced zone extends towards the south. North from this zone an iron-reducing zone and a zone with variable conditions have been observed. In the deepest layer the stronger reduced zone seemed to be moved northwesterly, in the direction of the groundwater flow.

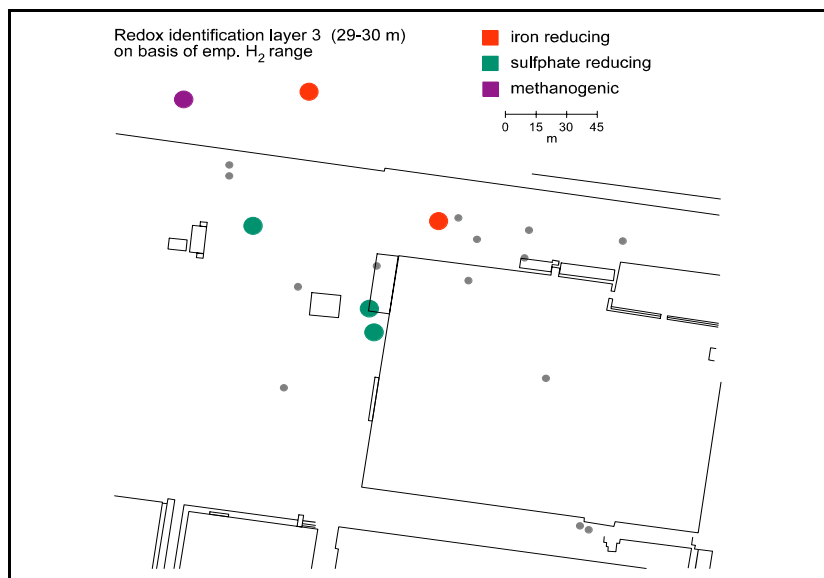
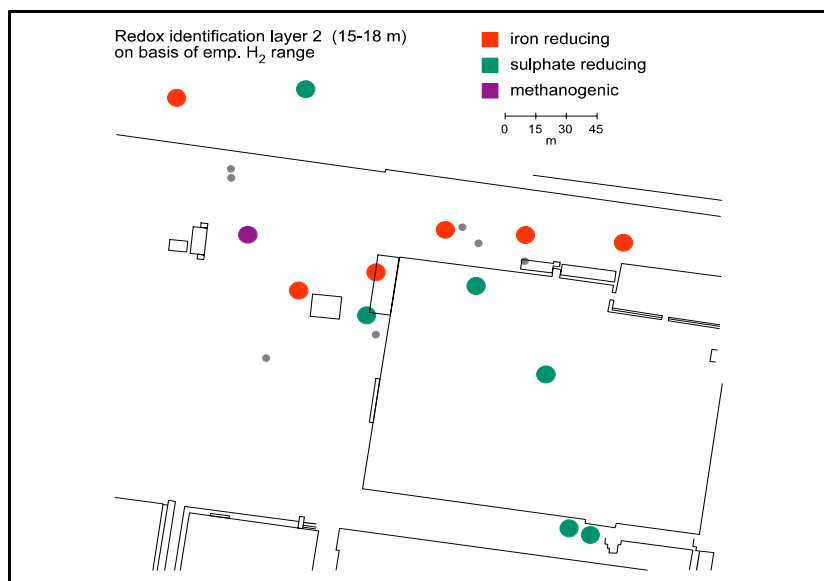
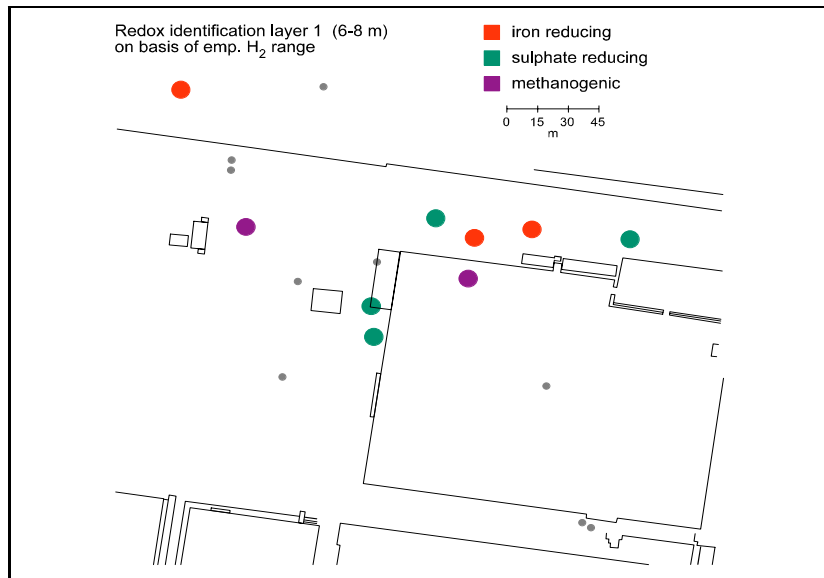


Fig. 34. Redox characterisation in layers according to the empirical hydrogen range

In the depth profile shown in figure 33 the spatial distribution with depth becomes more clear, and redox zones seem to be related to the contaminated zones. Basically, two major sources of contaminants can possibly account for more reduced conditions. A BTEX source at sampling point C40, and a DCA source at sampling point NOB2. Both type of contaminants can act as electron donor and are expected to reduce natural electron acceptors and consequently cause a drop in redox conditions. At both spots methanogenic conditions exist according to the empirical hydrogen method, while sulphate-reducing and iron-reducing conditions exist outside these zones. The deepest sampling point of NOB3 is also determined as methanogenic, and could be associated with the DCA contamination.

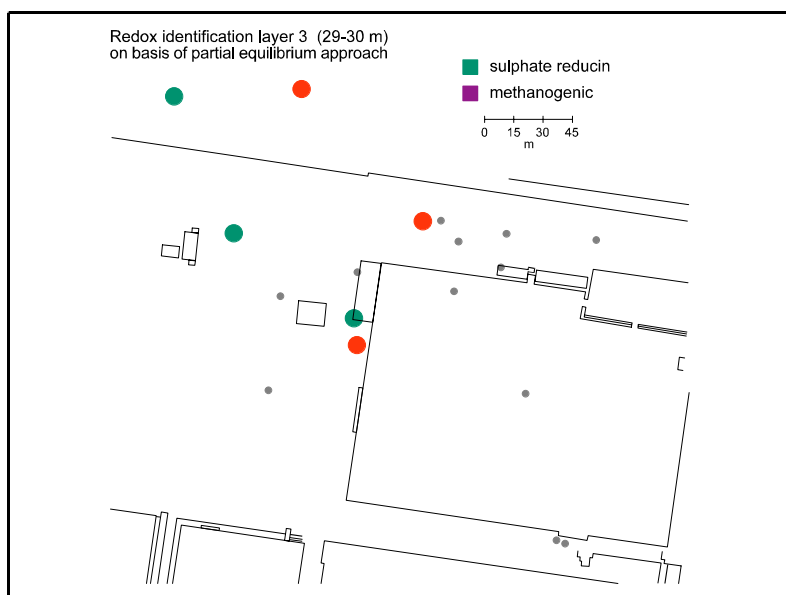
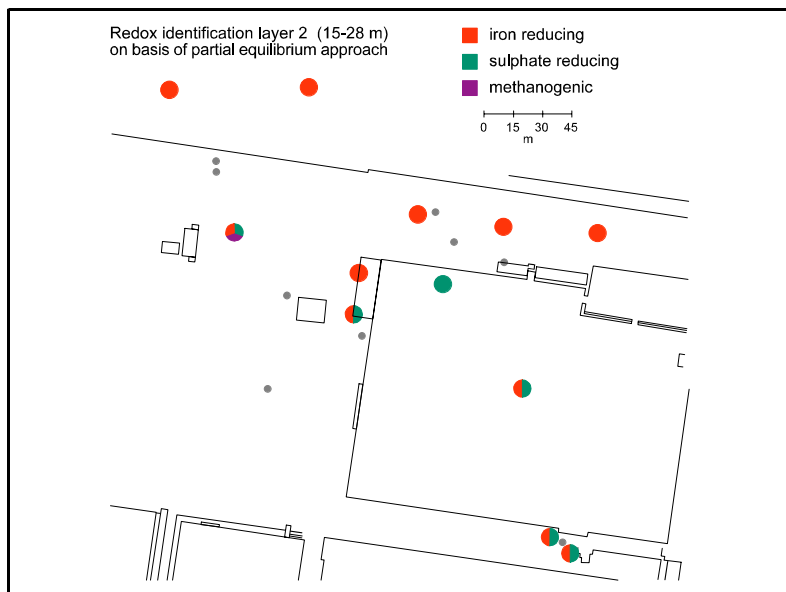
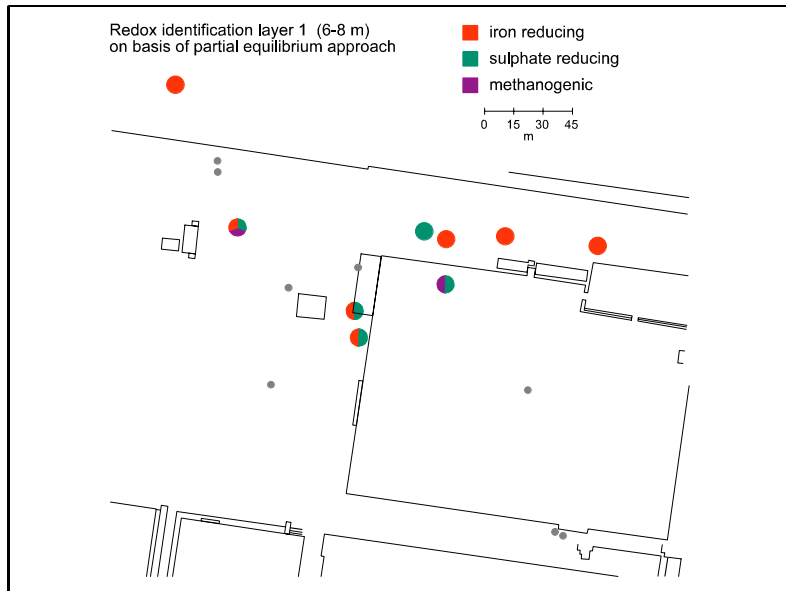
9.2.4 *Partial equilibrium approach*

The partial equilibrium approach is useful to determine for each sample which redox processes are favourable and might take place.

The groundwater at the DAF location has been analysed thoroughly for several different redox parameters and enough information is available to be able to use the partial equilibrium approach. The absence of oxygen and nitrate in the groundwater indicates that redox conditions are strongly reduced. Therefore only iron reduction, sulphate reduction and methanogenesis will be covered in the partial equilibrium approach. Manganese reduction is not considered to be an important process for reasons that are mentioned earlier, and is therefore not covered in this method.

For several sampling points Gibbs energies have been calculated for iron-reducing, sulphate-reducing and methanogenic reactions. Those calculations are based on the concentrations of hydrogen and redox species and also on pH and temperature. The calculations of the sulphate-reducing reactions are partly based on sulphide concentrations. On this location sulphide has not been analysed, but extrapolating is justified in this case. It appears that a large change in the sulphide concentration leads only to small change in the Gibbs energy of the reaction. At a few sampling points also bicarbonate concentrations had to be extrapolated, which has also been shown to be justified. The Gibbs energies that have been calculated for individual redox reactions form the basis for the identification of redox processes. Depending on whether this calculated Gibbs energy is below or above the threshold Gibbs energy, the reaction is considered as either favourable or unfavourable, respectively. Similar to the other locations, also at the DAF location a threshold Gibbs energy of -5 kJ/mol, has been chosen as critical value.

The partial equilibrium approach resulted in the redox characterisation shown in figure 35. For each layer of depth is indicated which redox processes are favourable. For some spots more processes might take place simultaneously. In the first layer various different redox conditions exist. In the centre a zone is present in which the redox conditions seem to be stronger reduced than in the surrounding area. In this zone sulphate reduction and methanogenesis might take place in addition to iron reduction. In the surrounding area sulphate reduction and methanogenesis are unfavourable and only iron-reducing conditions are expected. In the second layer a similar pattern has been found. In the same two wells where methanogenesis was favourable in the first layer, also in the second layer stronger reduced conditions exist. In the western situated well three redox processes are favourable and might occur simultaneously. On the other well only sulphate-reducing conditions are expected. In the south sulphate reduction and iron reduction are favourable and a combination of both processes might take place. In the northern part only iron-reducing conditions are favourable. At the deepest layer, a sulphate-reducing zone has been developed in the northeast. Possibly this zone has been moved from the central part of the location in the direction of the groundwater flow. Due to the limited amount of sampling points at this depth the redox conditions in the other parts could not be determined.



In the depth profile the same two stronger reduced spots become visible (see fig. 33). Apparently, more redox processes are favourable simultaneously at these spots. A local supply of electron donor could have raised the hydrogen concentration temporarily and thus enabling sulphate reduction and methanogenesis to take place, while trivalent iron is still available as electron acceptor. As soon as the electron donor supply ceases, the hydrogen concentration decreases and these reactions will become unfavourable again leaving iron reduction as the only process. It seems that the background redox conditions are iron-reducing, but sulphate-reducing conditions, or a combination of both occurs in the vicinity of the plume.

9.2.5 *Comparison of the methods*

Not all methods give similar results for the redox characterisation. Especially the macro chemical method is strongly different from the methods which are based on hydrogen concentrations. Overall, the redox conditions according to the macro chemical method are less reduced than for the other methods.

The macro chemical method is not considered to give reliable results for this location. The redox seor cobem(T

9.3 Hydrogen and dechlorination

In this section comparisons are made between dechlorination and hydrogen on one hand, and the redox conditions derived from hydrogen on the other. Also the relation between the type of electron donor and dechlorination processes is investigated. Similar to the other locations, also for the DAF location the Cl# is used to quantify the stage of dechlorination.

Thermodynamic calculations indicate that dechlorination reactions are energetically favourable throughout the location. All values are well below the reported threshold Gibbs energy for ATP-synthesis. For the different dechlorination reactions, a range is indicated with the minimum and maximum value of all samples (see table 12).

According to expectations, dechlorination of the higher chlorinated ethenes is energetically more favourable than dechlorination of lower chlorinated ethenes. The energy which is involved in DCE and VC dechlorination is in the same range, but slightly lower for VC dechlorination. Ethene reduction to ethane is far less favourable than the dechlorination reactions.

Table 12. The ranges of the calculated Gibbs energies for different dechlorination reactions with hydrogen.

dechlorination process	minimum observed Gibbs energy (kJ/mol)	maximum observed Gibbs energy (kJ/mol)
PCE dechlorination	-162	-135
TCE dechlorination	-152	-127
DCE dechlorination	-141	-110
VC dechlorination	-143	-122
ethene reduction	-77	-54

In principle, dechlorination reactions with hydrogen are considered favourable, but if dechlorination actually takes place still has to be proven. One of the ways to quantify dechlorination processes is the Cl# (see chapter 6). At the DAF location Cl# range between 1 and 2.5 which is considered to be very low. Dechlorination seems to be a very important process. In figure 36 Cl# have been plotted in the depth profile. A spatial trend of Cl# has been observed along the flow path. In the core of the chloroethene plume the highest Cl# are found, but along the flow path Cl# decrease, indicating that dechlorination takes place. According to the pattern of Cl#, the dechlorination process has taken place in all zones of the plume. Apparently, the redox conditions are favourable for dechlorination processes throughout the entire plume. Strong relationships between the Cl# and redox conditions have therefore not been found. Also a direct relationship between hydrogen concentrations and dechlorination has not been found (see fig. 37). The samples with the highest hydrogen levels (above 2 nM) do not have the lowest Cl#. So, the hydrogen concentrations found at the DAF location are all considered to be in a range where dechlorination processes take place, but no optimal range for dechlorination was detected. These results are in conflict with the results of Yang and McCarty [1998] which indicate an optimal hydrogen range for dechlorination between 2 nM and 10 nM. Most hydrogen concentrations found here are well below this range and imply that the conditions would be unfavourable.

Fig. 36. Spatial distribution of Cl#, indicating zones that are in different stages of dechlorination.

Since BTEX and DCA both might act as electron donors in dechlorination processes, the zones in which these compounds are present in large amounts are expected to stimulate dechlorination processes. This, however, does not seem to be the case at this location, since no association between BTEX and DCA sources and decreased Cl# have been found.

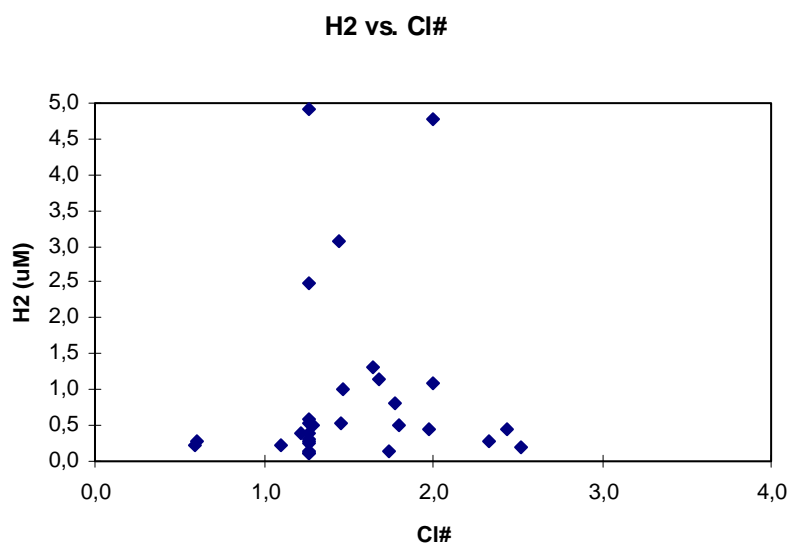


Fig. 37. Plot of hydrogen against Cl#.

From figure 38 can be concluded that no clear relationship is exists between hydrogen concentrations and the concentrations of dissolved organic carbon (DOC). It is expected that higher DOC levels cause an increase in the hydrogen concentrations, but only a very weak association can be found.

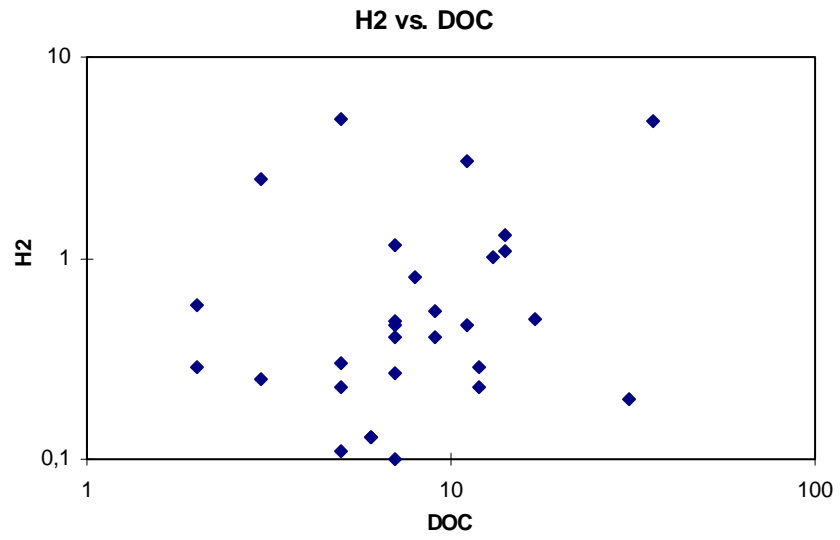


Fig. 38. Plot of hydrogen against DOC.

SBNS LOCATION

10.1 Description of the SBNS location

10.1.1 *Situation*

The site discussed in this chapter has been owned by the Dutch railroad company (Nederlandse Spoorwegen) for more than a century. The site covers an area of approximately 12 acres, and is located in the centre of the city Tilburg. The site has been used for maintenance activities of railroad material including cleaning, surface treatment, metal casting and paint spraying. Nowadays, the central part is still being used for the cleaning of engines and pipes. As a result of these activities the site has become contaminated with several different compounds, including chloroethenes, BTEX compounds, mineral oil, polycyclic aromatic hydrocarbons and heavy metals.

10.1.2 *(Geo)hydrology*

The top layer of the site is part of the Nuenen formation and is variable in thickness from 5 till 12 meters. The first aquifer, which is laying beneath the top layer, is the formation of Sterksel an Veghel. This formation reaches to a depth of 57 metres below ground level. The boundary between the upper layer and the first aquifer cannot be defined sharply because both layers strongly resemble in composition. The phreatic groundwater would normally flow in a northerly to northeasterly direction but due to a groundwater sanitation nearby, the groundwater flow is northwesterly directed.

10.1.3 *Description of the contamination*

High levels of BTEX and Chlorinated Solvents have been found out around sampling points 907 and 103. These points might be considered as the source and the core of a plume. A second BTEX plume is located northwesterly from the previous source, but the exact dimensions of this plume are not sufficiently known.

In the direction of the groundwater flow path, 11 sampling points have been arranged. The point labelled 251b is located upgradient in respect to the SBNS site but could not be considered to represent the background conditions, since considerable amounts of PCE, TCE and BTEX have been found here. From this point of view the sampling point 156-2 is more reliable in defining background conditions, since at this point all contaminants remain below the instrumental detection limit.

10.2 Redox characterisation

10.2.1 *Redox potential*

Similarly to the other locations, also at the SBNS location the redox potential will be used only for a spatial comparison to distinguish between reductive zones. Redox potentials have been measured for all sampling points and range between -75 mV and 312 mV (see fig. 39). The redox potential of 156 point, which might represent the background conditions, is 40 mV. In the core of the principal plume the lowest redox potentials have been found (between -75 mV and -50 mV), which is in accordance with the expectations. Due to the presence of contaminants that might act as electron donor (e.g. BTEX), natural electron acceptors become reduced, which leads to a drop in the redox conditions. For the other sampling points (251b, 107, 902-1, 902-2, 905 and A13-2) the redox values range between 145 mV and 312 mV. As expected, redox potentials, that have been determined in a simple standard way, can be considered inefficient to describe sharply the exact redox conditions that take place.

Pattern of redox potentials (Eh)

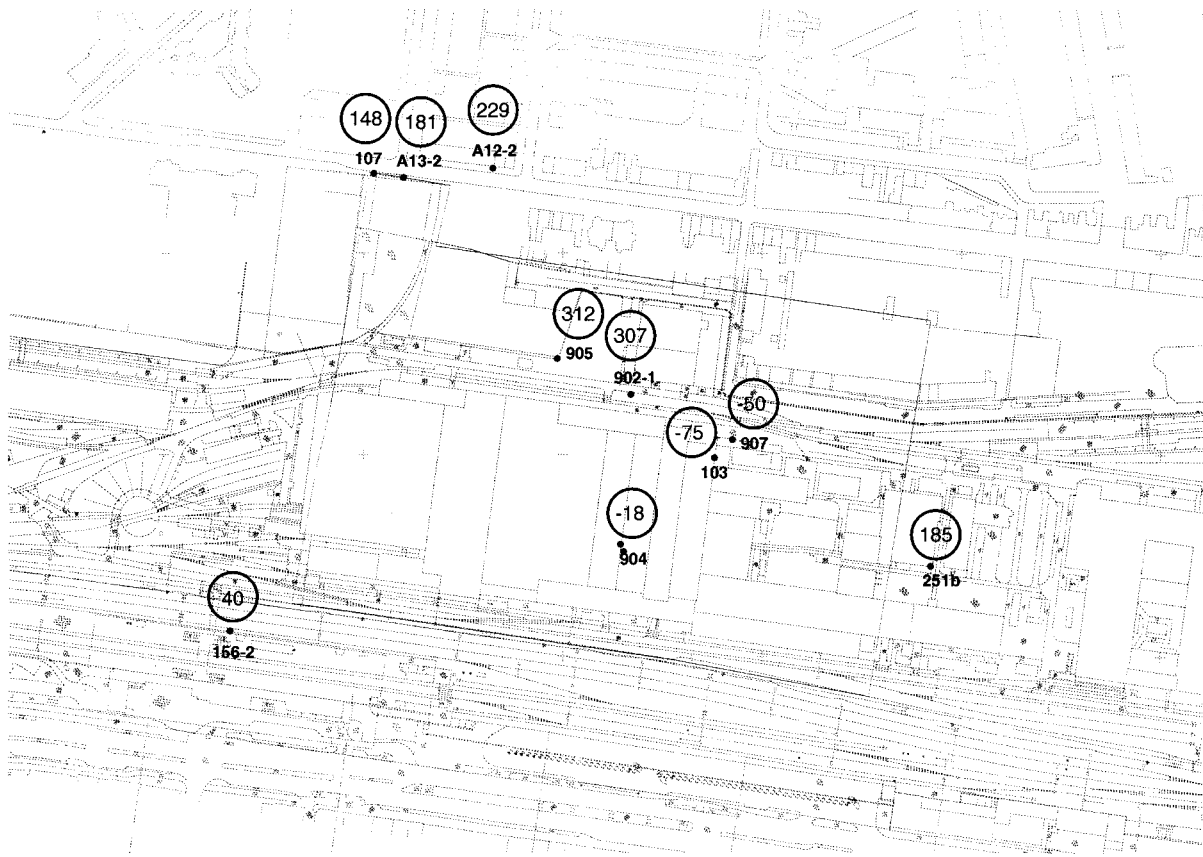


Fig. 39. Spatial distribution of redox potentials at the SBNS site Tilburg.

10.2.2 Macrochemistry

Several relevant species have been measured in order to identify the redox conditions but not all the species are useful for that aim. According to the criteria for a typical situation as used in the redox identification protocol (see chapter 6), the species considered are the following: O_2 , NO_3^- , Fe^{2+} , SO_4^{2-} and CH_4 (see fig. 40). The dataset is complete for most of the sampling points and sufficient to make a redox characterisation, except for sampling point A12-2 which has been neglected.

$CH_4 > 1 \text{ mg/l}$	→yes: methanogenic
↓	
$SO_4 < 1.5 \text{ mg/l}$	→yes: sulphate-reducing
$Fe(II) > 1.5 \text{ mg/l}$	
↓	
$O_2 > 1 \text{ mg/l}$	→yes: oxygen-reducing
↓	
$NO_3 > 0.5 \text{ mg/l}$	→yes: nitrate-reducing
↓	
no:	iron-reducing

Fig. 40. Criteria for macro chemical redox characterisation.

At the points labelled 907 and 103 the methane concentration is clearly higher than the critical value, indicating methanogenic conditions. The methane concentrations found were 2.6 mg/l and 1.4 mg/l respectively. At non-methanogenic areas, a decreased sulphate concentration and an

increased divalent iron concentration indicated sulphate-reducing conditions. Although divalent iron has only been measured three sampling points, it is safe to state that sulphate-reducing conditions have not been encountered throughout the site since sulphate concentrations are nowhere decreased (except at the methanogenic sampling points). For the sampling points where oxygen has been determined it is not encountered in significant amounts. Nitrate, on the other hand is found at sampling points: 904, 905, 251b, 902-1 and 902-2, and are therefore considered to be nitrate-reducing. According to the formulated criteria, the other sampling points (156-2, 107 and A13-2) are considered iron-reducing.

According to the macro chemical approach, it could be concluded that the core of principal plume, i.e. the most contaminated sampling points (i.e. 103 and 907), is characterised as methanogenic and the periphery as nitrate-reducing (see fig. 41). In the downgradient plume, including the wells 107, A13 2, and 156-2 iron-reducing conditions prevail. The point 156-2 has been considered to be under iron-reducing conditions. Comparing the assumed background conditions with the conditions in the periphery of the principal plume, it is expected that an influx of nitrate has taken place. According to the available data it is not possible to assess if the influx is temporary, e.g. through rain infiltration or a sewer leak.

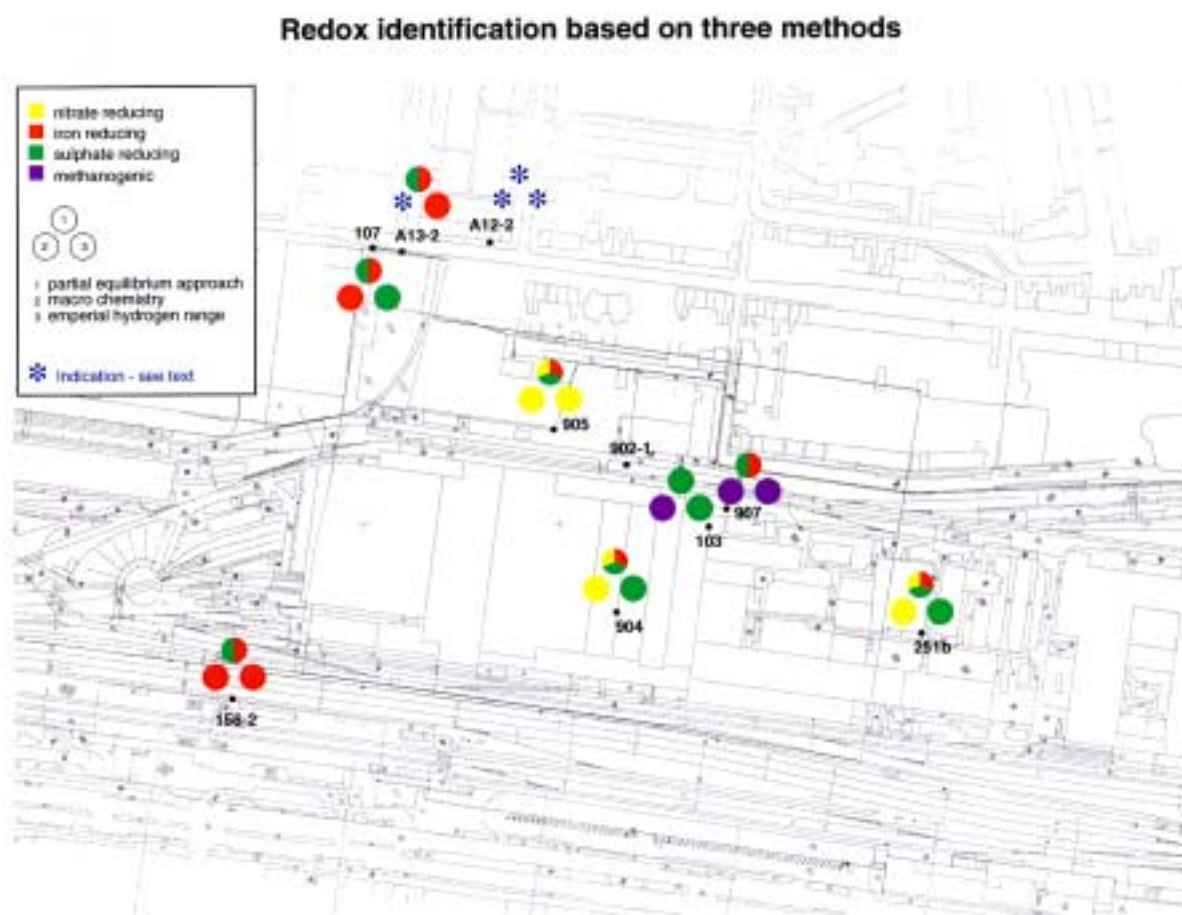


Fig. 41. Overview of the redox characterisations according to three different redox identification methods: macro chemical, empirical hydrogen and partial equilibrium approach (see legenda). * means that data were incomplete.

10.2.3 Comparison with empirical hydrogen range

The hydrogen concentration and temperature have been measured throughout the entire site. The H_2 -concentrations range between 0.16 nM and 2.14 nM (see table 13) and the temperature between 11.5 °C and 17.1 °C. This temperature fits with the temperature of the hydrogen range

that applies to most situations between 10 °C and 15 °C. This range is shown in table 14 and explained in chapter 4.2.1.

Table 13. Hydrogen analysis for different sampling points.

sampling point	[H ₂] in nM	sampling point	[H ₂] in nM
156-2	0.28	905	0.16
251b	0.42	107	0.59
907	2.14	902-1	0.15
103	0.31	A12-2	-
904	0.37	A13-2	0.25
902-2	0.31		

Table 14. Criteria for the empirical hydrogen method.

hydrogen concentration		redox condition
H ₂ ≤ 0.2	→	nitrate-reducing
0.2 < H ₂ ≤ 0.3	→	iron-reducing
0.3 < H ₂ ≤ 1.5	→	sulphate-reducing
H ₂ > 1.5	→	methanogenic

In this way two sampling points have been classified as nitrate-reducing, two as iron-reducing, five as sulphate-reducing and only one as methanogenic (see fig. 41). The most reduced spot is found at sampling point 907, at which methanogenic conditions appeared to exist. Around this point a sulphate-reducing area has been identified (point 103, 904 and 902-2) and a little further, downgradient, a nitrate-reducing zone (point 905 and 902-1). At sampling points 156-2, 107 and A13-2, iron-reducing, sulphate-reducing and iron-reducing conditions have been found, respectively.

10.2.4 Partial equilibrium approach

Gibbs energies have been calculated for several relevant redox reactions. Some reactions have not been covered. Manganese reduction has not been considered since manganese hydroxides are not sufficiently present in Dutch soils to be an important electron acceptor. Since sulphide concentrations were always below the instrumental detection limit, it has been assumed that sulphides precipitated to iron sulphides as soon as they were produced. No reaction in which sulphate reduces to sulphide has therefore been included. Instead, the reaction in which sulphate reacts directly to iron sulphide is considered.

In order to estimate the nitrate-reducing reactions, the nitrogen concentration has been assumed to be at maximum solubility ($5.15 \cdot 10^{-4}$ M). Bicarbonate concentrations have not been measured, but extrapolations of this compound have been made and have been justified since large concentration differences have only a minor effect on the calculated Gibbs energy. For the iron-reducing reaction, goethite has been considered as the predominant iron mineral. Also for iron-reducing reactions extrapolations had to be made, since divalent iron concentrations have only been measured at a few sampling points. For some points extrapolations were not justified and no characterisation could be made.

The Gibbs energies which have been calculated for the individual redox reactions are compared to the threshold Gibbs energy of -5 kJ/mol in order to determine if the reaction is favourable or unfavourable. Arguments for the selection of this value have been given in chapter 6.

For all sampling points where nitrate is detected, the nitrate-reducing reaction can be considered as energetically favourable (see fig. 41). The calculated Gibbs energies are around -180 kJ/mole, which is well below the threshold value. So nitrate-reducing conditions have been shown to be favourable for the sampling points 904, 902-1, 902-2 and 905. According to the partial equilibrium approach at most parts, more processes are favourable simultaneously. Methanogenesis is not considered to be favourable in any part of the site. In the core of the combined chloroethene and BTEX plume, sulphate-reducing conditions exist. West from this zone nitrate-reducing conditions are favourable as well as iron- and sulphate-reducing conditions. Apparently, an influx of nitrate is not capable to suppress the hydrogen concentration to a level that excludes the other reactions. Either it is a temporary influx or the supply is too small. In both cases a situation of non-steady-state is developed. In the other parts of the site a combination of iron- and sulphate-reducing processes is favourable.

10.2.5 *Comparison of the methods*

Although small differences exist between the redox identification methods, they all show the same sequence of redox zones. All methods have identified a sulphate or methanogenic zone around 103 and 907, which is associated with the BTEX contamination. West from this area, wells 905 and 902 mark a zone where an influx of nitrate has caused nitrate-reducing conditions. At 904 and 251b less consistent results have been found for the macro chemical and empirical hydrogen methods. In this situation the partial equilibrium approach has shown to be very useful, since it provides results that are consistent with the those of the other two methods. At 904 and 251b both the macro chemical method and empirical hydrogen method indicate conditions that have been determined as favourable by the partial equilibrium approach. In the western zone with sulphate- and iron-reducing conditions all methods are consistent with each other.

In contrast to the other redox identification methods the partial equilibrium approach was able to identify multiple redox conditions typical for redox transition zones. Since this appears to be the case in many parts of this site, the partial equilibrium approach was not very discriminative with respect to identifying the dominant redox process.

10.2.6 *Conclusion for redox characterisation*

In general, the four redox identification methods give different redox results, at the level of individual sampling points. In contrast, all the methods produce the same pattern, a similar sequence of redox zones. Comparing the macro chemical and empirical hydrogen method, both procedures characterise the periphery of the plume and the more reduced core zone similarly. Both methods could not account for simultaneously favourable redox conditions as often found in redox transition zones. For such areas the partial equilibrium approach appears to be a better method. On the one hand the partial equilibrium approach gives a more detailed picture of the prevailing redox conditions, on the other hand it gives a less discriminative result.

Due to a lack of data, several assumptions and extrapolations had to be made in order to apply the partial equilibrium approach. An improved performance of this method is expected if more wells are included and more parameters are measured. According to the results of this case study, the empirical hydrogen method appears to be a valid detection method at least for a first screening investigation. The partial equilibrium approach can be used for improved interpretations, especially in redox transition zones.

10.3 **Hydrogen and dechlorination**

The aim of this paragraph is not to assess the distribution of contaminants at SBNS site, but to understand if there is any correlation between the hydrogen concentration and lines of evidence of dechlorination. Also the relationship between hydrogen and the type of carbon source as prin-

cipal electron donor is being investigated. Comparisons between dechlorination and hydrogen and electron donor source are being made in location maps.

Dechlorination processes are expected to be more favourable under reduced redox conditions than under less reduced conditions. So based on this consideration it is expected that at the SBNS site most dechlorination takes place in the core of the contaminated plume (907 and 103), where the concentration of both the total chlorethenes and BTEX are highest and where sulphate-reducing and methanogenic conditions exist. Patterns of the Cl# show that this is indeed the case.

In figure 42 the hydrogen concentration is plotted. In the core or the plume the concentrations of hydrogen are around 2 nM while at the periphery much lower values have been observed. When comparing this hydrogen pattern with the Cl# (see fig. 43), it becomes clear that in zones where high hydrogen concentrations are found, Cl# remain low (lower than 2). This suggests that high hydrogen concentrations favour the dechlorination process. It seems that these observations are in accordance with the reported range of optimal dechlorination between 2 nM and 11 nM [Yang and McCarty, 1998].

Fig. 42. Spatial distribution of hydrogen concentrations at the SBNS site.

Fig. 43. Spatial distribution of chloride number at the SBNS site.

Fig. 44. Spatial distribution of BTEX concentrations at the SBNS site.

Fig. 45. Spatial distribution of total chloroethene concentrations at the SBNS site.

Further spatial comparisons have been made with the plume dimensions of BTEX and chloroethenes. In figure 44 and 45 is seen that the chloroethene plume and the BTEX plume partly overlap. Since BTEX compounds might act as primary carbon source, they can be fermented to produce hydrogen. It is therefore expected that in zones where BTEX compounds are found, hydrogen concentrations are also increased. For well 107, however, increased BTEX concentrations have only led to a small increase of hydrogen concentrations.

10.3.1 *Conclusion of dechlorination*

In conclusion it appears that there is a very close correlation between hydrogen and BTEX on one hand and dechlorination on the other. High hydrogen concentrations (around 2 nM) which might have been caused by the presence of BTEX, seems to stimulate dechlorination processes.

This case study could be considered as a good starting point, but more analytical data are required to support a statistical interpretation and a validation of hydrogen as a tool to evaluate dechlorination.

BANISVELD LOCATION

11.1 Description of the Banisveld location

11.1.1 *Situation*

The Banisveld location is a former landfill southwestern of Boxtel (the Netherlands). From 1965 to 1977 and in 1990 and 1991 several types of waste have been dumped, including household, building, industrial and possibly chemical waste. As a result a variety of different pollutants have contaminated the soil and groundwater. In the groundwater some of these compounds are very mobile and form a potential threat for a nearby nature reserve.

11.1.2 *(Geo)hydrology*

The Banisveld location is situated in a region where the Nuenen formation and the formation of Sterksel form the upper parts of the subsurface. The Nuenen formation is geologically complex and consists of alternating layers of fine sands, loam, and peat. The formation of Sterksel consists of gravels and sands and forms the first aquifer. At the Banisveld location the Nuenen formation forms a top layer of 15 to 25 metres thickness. To a depth of 10 metres below groundlevel fine sands are locally alternated by a peat or loam layer. From 10 to 16 metres below groundlevel a loam layer is present together with layers of sand. Sand is found below 16 metres. The groundwater flow is strongly influenced by both the complexity of this formation and seasonal variations. During the winter the groundwater level is high and groundwater from the top layer drains in surface waters like the Heilooop. During the summer when the groundwater level is low the Heilooop infiltrates its water to the deeper layers mainly in the direction of Smalbroeken. Additionally, a water flow is observed from the first aquifer to the Nuenen formation.

11.1.3 *Contaminated situation*

In previous research increased concentrations of macro chemical contaminants (chloride, chemical oxygen consumption, nitrogen, ammonium etc.), heavy metals, aromatics and chlorinated solvents have been found in the groundwater. The spreading of these contaminants is determined by the groundwater flow over years, which is a combination of winter and summer variations. In a recent project the dimension of the contaminated plume have been characterised (Boris van Breukelen, in preparation). Also the potential for natural attenuation has been determined (NOBIS project 95-2-09).

11.1.4 *Arrangement of the wells*

Eleven wells have been placed in a transect along the groundwater flow path (see fig. 46). Well p10 and p9 are considered to represent the background conditions and the source of the contaminated zone, respectively. At different depths until 10 meters, samples have been taken from these wells. In this way it was possible to make a cross-section which has been used for the redox characterisation.

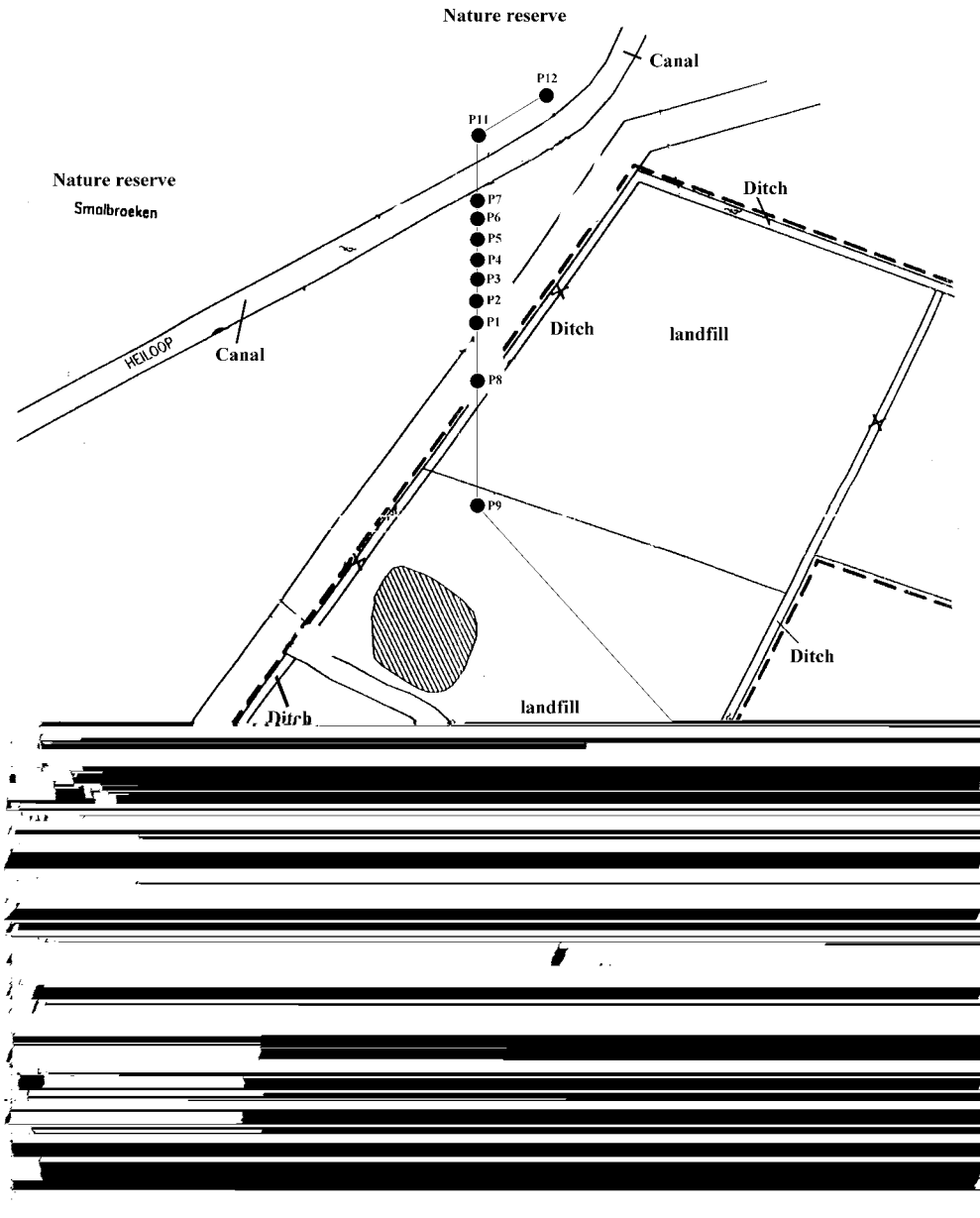


Fig. 46. Map of the location including the arrangement of the wells and the transect.

11.2 Identification of the redox conditions at the Banisveld location

In the Banisveld case the use of hydrogen will be considered as a method to identify the local redox conditions. Two different approaches that use hydrogen will be applied on this site. The first method is based on hydrogen concentration ranges, which have been determined empirically. The second is called the partial equilibrium approach and is based on both hydrogen concentrations and concentrations of several redox species. These approaches will be validated by comparing the result to the macro chemical method and the processes in the contaminated plume. Redox potentials have not been measured at this site.

11.2.1 Macrochemistry

On basis of the various species that have been measured, redox conditions could be identified at the Banisveld location. The criteria that have been used for this location are shown in figure 47. These criteria have been determined in a site-specific way instead of the generalistic criteria for a

typical location using the standard redox identification protocol (see chapter 6). For setting the criteria not all species were useful, in fact, only nitrate, sulphate and methane have been used. Since the Banisveld site is a landfill, also several other contaminants are present that could have initiated several different processes and could have caused increased background concentrations of redox species like methane, sulphate, divalent iron. In this site-specific approach these increased concentrations are taken into account, by increasing the critical values and by eliminating divalent iron as criterion.

NO ₃ > 1.5 mg/l	→	nitrate-reducing
↓		
SO ₄ > 50 mg/l	→	iron-reducing
↓		
SO ₄ < 50 mg/l	→	sulphate-reducing
CH ₄ < 1 mg/l		
↓		
SO ₄ < 50 mg/l	→	methanogenic
CH ₄ > 1 mg/l		

Fig. 47. Criterial for the macro chemical redox identification method.

No significant amounts of oxygen have been found at the Banisveld location, indicating that oxygen-reducing conditions do not take place. The presence of significant amounts of nitrate is characteristic for nitrate-reducing conditions. Two groups can be identified: a group in which nitrate was absent or present in very small amounts (0 - 0.4 mg/l), and a group in which nitrate is present in relatively large amounts (above 17 mg/l). Conveniently, a certain critical value has been used which in this case is 1.5 mg/l. If the conditions are not nitrate-reducing, sulphate and methane can be used to make a further distinction between iron-reducing, sulphate-reducing, or methanogenic conditions. High sulphate concentrations indicate that sulphate reduction has not (yet) taken place and low concentrations that sulphate reduction might have taken place. Similarly, high methane concentrations are associated with methanogenesis. The determination of critical values for sulphate and methane is less straightforward as for nitrate. No clear distinction between low and high concentrations could be found, possibly due to local heterogeneity. Although there is a high probability of misinterpretation, critical values had to be determined and implemented in order to use this method. Based on the distribution of these parameters, a reasonable critical value for sulphate is 50 mg/l and for methane is 10 mg/l.

In figure 48 redox characterisations according to the three redox identification methods are shown.

For all sampling points redox conditions have been identified using these criteria. Different redox zones can be identified: a strongly reduced zone is located inside the contaminant plume. Although methanogenic conditions seem to dominate this zone a serious probability of misinterpretation exists due to the transport of methane. Possibly, methane has been produced in the core of the landfill where truly methanogenic conditions exist and has subsequently been transported along the groundwater flow to zones in which sulphate-reducing conditions exist. Therefore these zones could have been falsely characterised as methanogenic. A more oxidised zone dominated by nitrate-reducing conditions has been located outside the plume at shallow depth. Sulphate- and iron-reducing conditions are found in deeper zones and possibly mark the background redox conditions.

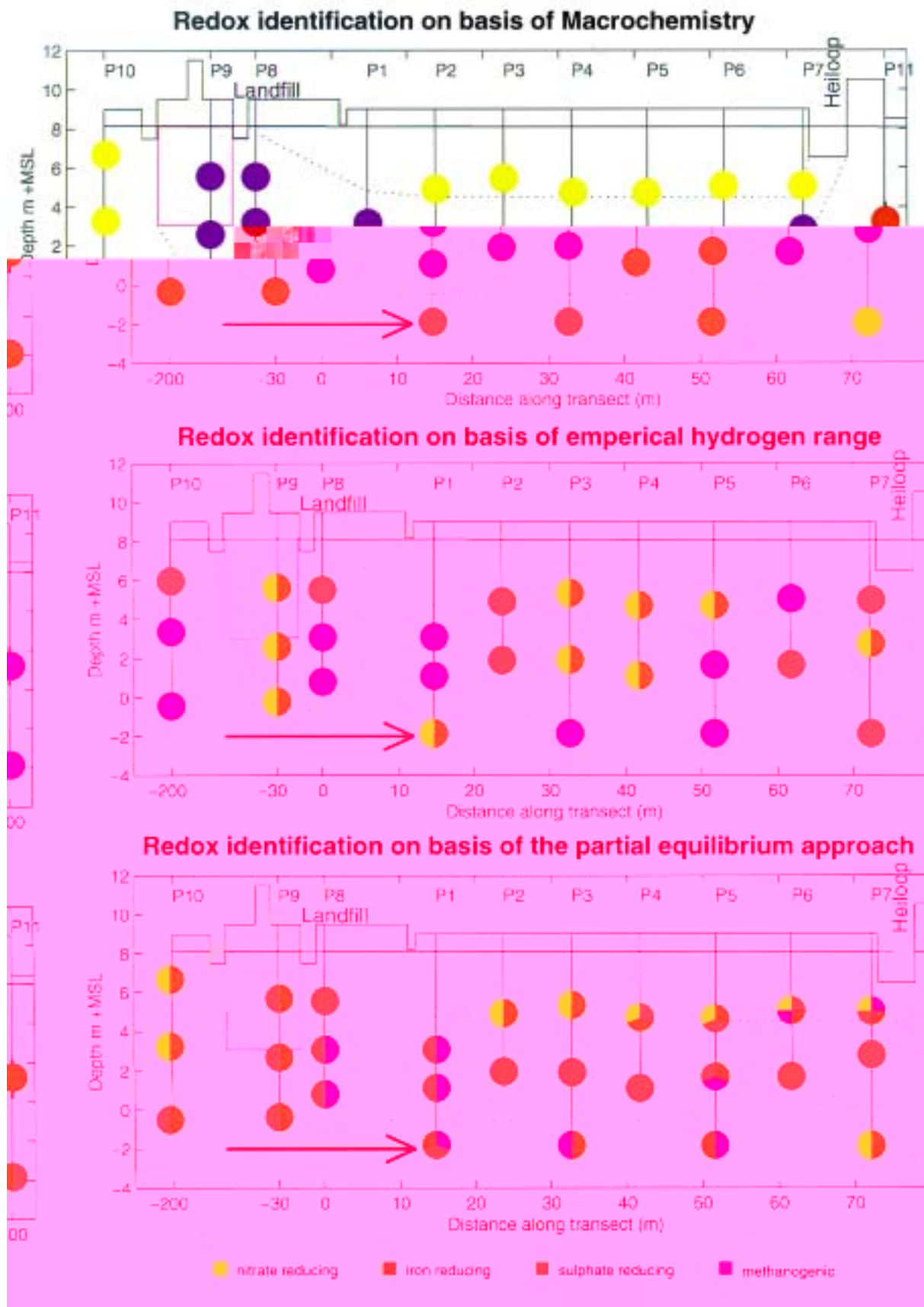


Fig. 48. Spatial distribution of redox conditions according to the three methods.

11.2.2 Empirical hydrogen ranges

At the Banisveld location hydrogen has been measured throughout the entire site. Solely by comparing the hydrogen concentration to an empirically determined range, redox conditions could be identified. The following critical values have been chosen as criteria (see table 15).

Table 15. Criteria for the empirical hydrogen method.

hydrogen concentration		redox condition
$H_2 < 0.7 \text{ nM}$	→	iron- or sulphate-reducing
$0.7 \text{ nM} < H_2 < 5 \text{ nM}$	→	sulphate-reducing
$H_2 > 5 \text{ nM}$	→	methanogenic

These criteria are distinct from the standard criteria used for situations between 10 °C and 15 °C (see table 4, section 4.2.1). When applying these standard criteria to the hydrogen concentrations at the Banisveld site, no discriminative results were obtained. The majority of the sampling points would in this way be identified as methanogenic or sulphate-reducing, while also nitrate- and iron-reducing conditions are expected (see section 11.2.1). A reason to deviate from the standard criteria could not be found, since the temperatures at the location seem to fit the indicated range. Surprisingly, the criteria do perfectly fit to empirical ranges that are based on experiments done at standard temperatures (25 °C). Possibly, the high organic carbon loads percolating from the landfill into the subsurface have created non-steady-state conditions. Hydrogen levels may not be associated with dominant redox processes. Instead of using the standard criteria, criteria were based on the distribution of measured hydrogen concentrations. In figure 49 is shown that the hydrogen concentration is distributed into three distinct intervals, representing different redox processes. Values between these zones have been used as the critical hydrogen concentrations.

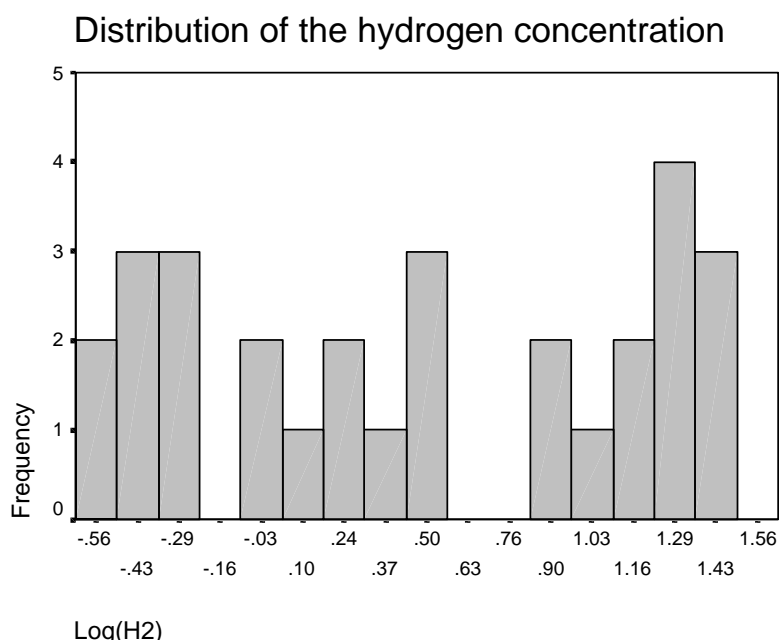


Fig. 49. Distribution of hydrogen concentration into three distinct groups.

The group with the highest hydrogen concentrations is considered methanogenic, the one with intermediate hydrogen concentrations sulphate-reducing, and the one with the lowest hydrogen concentrations corresponds to iron-reducing or nitrate-reducing conditions. A further discrimination between nitrate-reducing and iron-reducing conditions could not be made within this

group, because not enough variation has been found between the values. This automatically leads to a reduction of specificity and performance of this method.

The redox zones with similar conditions that have been identified are shown in figure 48. Although there is a strong variation, redox conditions can be recognised. No logical explanation could be found for the position of the different redox zones. A less reduced zone involving nitrate- and iron-reducing conditions is present in the core of the landfill and between p3 and p5 close to the surface, indicating a possible influx of nitrate rich water (i.e. through rain or other infiltration). More reduced conditions i.e. sulphate-reducing and methanogenic conditions, exist in other parts of the site.

11.2.3 *Partial equilibrium approach*

Because of the numerous measurements that have been done, a redox identification could be made following the partial equilibrium approach. Based on the concentration of hydrogen and redox species in combination with temperature and pH, Gibbs energies have been calculated for several relevant redox reactions. Depending on whether the calculated Gibbs energy is below or above the threshold value, the reaction can be considered favourable or unfavourable, respectively. Similarly to the other locations a value of -5 kJ/mol has also been selected as threshold for the Banisveld location.

The results of the partial equilibrium approach have led to a pattern in which all reactions are indicated that are considered favourable (see fig. 48). Apparently, on several parts of the site, for example in the shallow parts, different redox processes are favourable and can take place simultaneously. The possibility that more reactions take place simultaneously at this location is very likely. Redox transition zones are expected when variations in the supply of electron acceptors and donors occur. A temporal influx of nitrate together with infiltrating rainwater in the upper part of the soil, might account for a combination of different processes when nitrate-reducing bacteria are unable to lower the hydrogen concentration. Similarly, a temporary increase in the amount of electron donor due to a local influx of an anthropogenic carbon source can lead to temporary increased hydrogen concentrations. Due to such an increase even the less favourable reactions might become favourable. As soon as the hydrogen level drops, these reactions become less favourable again and stop.

More uniform redox conditions have been found in the contaminant plume where sulphate-reducing conditions are favourable, and sometimes in combination with iron-reducing or methanogenic conditions.

11.3 **Comparison of the different redox identification methods**

The results of the different methods that have been used to identify redox conditions do not closely match. A very large difference between the macro chemical method and the empirical hydrogen range has been found. Although it does not indicate the relative importance and dominance of redox processes, the partial equilibrium approach is more specific than the other methods since it indicates all processes that are favourable and might occur. Moreover, the partial equilibrium approach is less dependent on arbitrary criteria used for discriminating redox conditions. It is therefore a more generic method not dependent on site specific conditions. By comparing the macro chemical and empirical hydrogen redox interpretation to the redox processes that are indicated as favourable according to the partial equilibrium method, interpretations that are not very likely from a thermodynamic point of view will become clear. It appears that for the macro chemical method several interpretations are not supported by thermodynamics, since the identified processes were shown to be thermodynamically unfavourable and therefore not likely to take place. Especially for the more reduced conditions the macro chemical method fails. Nitrate-reducing conditions have been determined correctly, which is logical since

nitrate-reducing conditions will always be determined as being favourable as long as nitrate is present.

Many interpretations have been made using the empirical hydrogen method, which are also inconsistent with the results of the partial equilibrium approach. Especially the characterisation as nitrate-reducing is often not supported by thermodynamics, indicating an insensitivity of hydrogen for nitrate-reducing conditions. Samples that have been identified as sulphate-reducing or methanogenic with the empirical hydrogen method seems to be unfavourable according to the partial equilibrium approach. And vice versa, at points that have been identified as nitrate- or iron-reducing, only sulphate-reducing conditions are considered favourable. The expected correlation between reduced redox conditions and the contaminated plume does not exist for the redox characterisation according to the empirical hydrogen method.

11.4 Relation between hydrogen concentration and type of carbon source

This section will focus on the association between hydrogen and the type of carbon source. Since many carbon compounds might be fermented to hydrogen and produce different hydrogen levels, an correlation between the carbon source and hydrogen concentration is expected. At the Banisveld site this might be of particular interest since many different carbon compounds are present here.

However, from the two plots (see fig. 50 and 51) it does not become clear that there is a relationship between hydrogen concentrations and DOC level or BTEX concentrations, respectively. Possibly, the actual hydrogen concentration is not only determined by the production of hydrogen by carbon sources, but also by the consumption by electron-accepting processes.

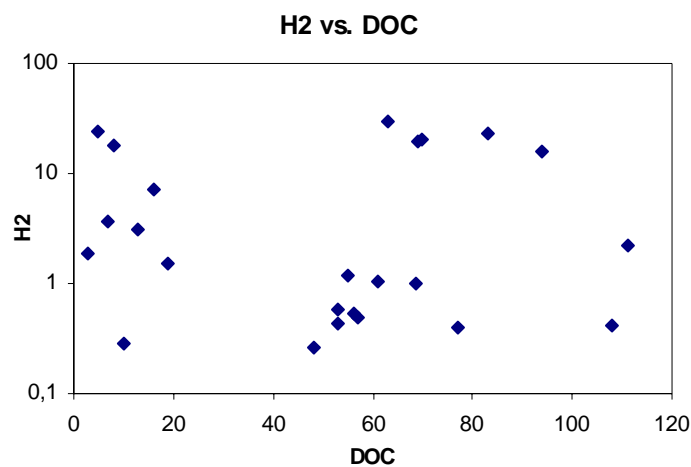


Fig. 50. Plot of hydrogen against DOC.

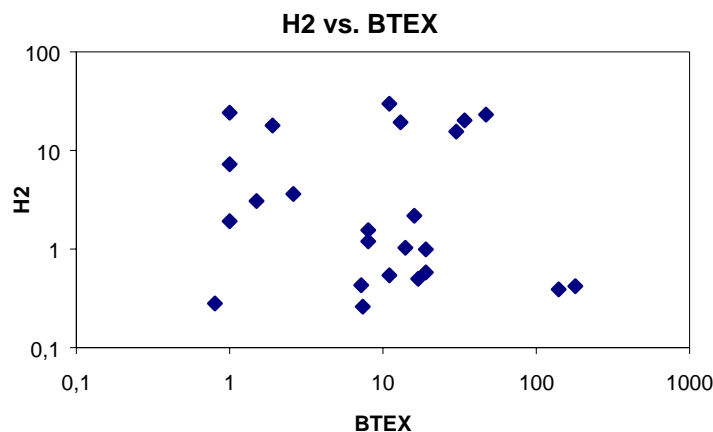


Fig. 51. Plot of hydrogen against BTEX.

11.5 Conclusions

The partial equilibrium approach has been proven to be a relatively site independent redox characterisation method. The macro chemical and empirical hydrogen method dependent on site-specific criteria and provided inconsistent results with the partial equilibrium approach. Both methods have been shown to determine redox conditions that from a thermodynamic point of view are unfavourable and not likely to take place. These methods are therefore considered as less useful for identifying the redox conditions at the Banisveld site. The redox identification made by the partial equilibrium approach appears to be most consistent. Additionally, the partial equilibrium approach is able to identify zones where more processes might take place simultaneously. These zones are very likely to be formed at this location, since a non-steady-state situation is expected as a result of a changing supply of electron donors and acceptors. The redox potential is partly supporting the partial equilibrium approach.

Summarising it may be concluded that the redox conditions are generally more reduced inside the contaminated plume than outside. The (temporary) influx of nitrate in the shallow regions close to the surface seems to influence the local redox conditions strongly. Furthermore the conditions inside the plume seem to be in a steady-state situation, since in many cases only one reaction is favourable at the same time. This is in contrast to transition zones in which more redox conditions are favourable simultaneously. For the Banisveld location the partial equilibrium approach has been proven to be to only method to produce a consistent redox identification.

No clear relation has been found between different carbon sources and the hydrogen concentration.

SITE COMPARISON

The applicability of the different redox identification methods strongly depends on the location. For all locations, the partial equilibrium approach has been shown to be a very useful tool to identify the redox processes that can take place and to provide a less site specific dependent reference for the other methods that have been used. In contrast to the other methods, the partial equilibrium approach was able to indicate redox transition zones where more redox processes take place simultaneously. In other words it is applicable for all types of locations and gives the most specific results. An additional advantage is that the same criteria can be used for all locations and do not have to be formulated for each location separately. Therefore, the method is more objective than the other methods and less affected by the scope of the researcher. A major disadvantage is that the partial equilibrium approach is not always discriminative. It does not pin point one single dominant redox process. This was most pronounced at many parts of the Banisveld location and the SBNS location.

The performance of the other redox identification methods was more strongly depending on the type of location. The Rademarkt location is the location where the most redox identification methods were consistent with each other. Except for Eh, all other methods gave a correct redox characterisation. Apparently, the conditions at the Rademarkt are at least close to steady-state, implying that the supply and consumption of electron donors and electron acceptors are in balance. Low DOC values indicate that electron donor limitation exist and redox processes take place in sequence. This is directly reflected in the presence of redox species and hydrogen levels which validates the macro chemical method and the empirical hydrogen method at this location.

At the DAF location the redox identification according to the empirical hydrogen method was in accordance with the partial equilibrium approach. The macro chemical method gave less satisfying results, since difficulties were encountered by the formulation of the criteria. Apparently, steady-state redox zones have not been developed sufficiently to affect the concentrations of the redox species. Also highly fluctuating background concentrations of these species could be the reason for the failure of this method. Hydrogen concentrations, which adapt more easily to a change of redox conditions, have been shown to be less influenced by non-steady-state situations, possibly present in parts of the site. In these situations, however, the specificity is not as high as for the partial equilibrium approach. This is most pronounced in the contaminated zones where a large supply of electron donor causes a temporary situation in which more redox processes take place simultaneously, but this could not be indicated by the empirical hydrogen method.

At the SBNS location all redox identification methods gave a more or less similar pattern, with strongly reduced conditions in the core of the contaminated plume and less reduced conditions outside and at the edges of the plume. However, a complete fit between the results of the various methods has not been found. The results of the macro chemical and the empirical hydrogen method are not always consistent, and the partial equilibrium approach was not always discriminative in these cases. The fact that the different redox identification methods indicated comparable general trends, could be an indication that the redox species, the steady-state hydrogen concentration and the redox potential responded reasonably well to changing conditions at the site.

The Banisveld location is an example of a location where both the macro chemical method and the empirical hydrogen method do not give a correct redox characterisation. The partial equili-

rium approach indicates that at many parts more redox processes occur simultaneously and the site can therefore be considered to be in a non-steady-state situation where the supply and consumption of electron donors and acceptors is not in balance. As a result of the various carbon sources that exist in the landfill the electron donor supply is expected to be highly fluctuating. In a same way an influx of nitrate could influence the electron acceptor supply and cause a non-steady-state situation. The presence of redox species on which the macro chemical method is based might therefore not reflect the occurrence of the actual redox processes, but the ones that have taken place. Also transportation of species like methane seriously limits this method. The non-steady-state situation affected the hydrogen concentration in such a way that hydrogen concentrations did not correspond to the redox processes that are taking place, but are the result of temporal fluctuations.

Summarising it can be stated that the performance of the various redox identification methods is (partly) determined by the extent to which a location is in steady-state. At locations where steady-state conditions are approached (Rademarkt), the macro chemical and empirical hydrogen methods are considered to be validated redox identification methods. At locations that are far from steady-state (Banisveld), the redox conditions could not be identified using these methods and only the partial equilibrium approach gave the consistent results. For locations that are somewhere in between those extreme situations, the validation of the macro chemical and empirical hydrogen method is less straightforward and both methods might characterise the redox conditions partly in a correct way (DAF and SBNS).

Table 16. Overview of the applicability of different redox identification methods on the four locations that have been studied.

location	redox potential	macrochemistry	empirical H ₂ -range	partial equilibrium approach
Rademarkt	-	+	+	++
DAF	+/-	-	+	++
SBNS	+/-	+	+	(*)
Banisveld	not measured	-	-	++

- no consistent pattern
- + consistent pattern; indication of dominant process
- ++ consistent pattern; indication of simultaneous occurring processes
- (*) not enough data

Dechlorination processes have been studied at three locations: Rademarkt, DAF and SBNS. According to the Cl#, dechlorination takes place at these three locations, but in some parts of the location more than in others.

For the SBNS site a close association exists between dechlorination processes, redox conditions, hydrogen concentration and the type of carbon source. In some parts of the site due to the presence of BTEX compounds that acted as electron donor, decreased redox conditions have developed and resulted in increased hydrogen concentrations. This situation has been favourable for dechlorination processes. In other parts where this situation has not been present, less dechlorination has been taken place.

At the other two sites no such strong relations have been found for dechlorination processes. At the Rademarkt site only indications have been found that at relatively high hydrogen concentrations as well as under methanogenic conditions, dechlorination plays an important role. A significant relation between hydrogen levels and DOC has been found.

Also at the DAF location hydrogen concentrations are related to the presence of electron donor sources like 1,2-DCA and BTEX. In the plumes of these compounds increased hydrogen concentrations and reduced redox conditions have been observed. A relation with dechlorination could, however, not be found, probably because the conditions are favourable for dechlorination processes throughout the entire location. This is supported by the fact that no nitrate-reducing conditions have been observed here. At the other two locations, these conditions did occur and might have suppressed the dechlorination process.

CONCLUSION AND OUTLOOK

As stated in the introduction, measuring hydrogen concentrations may be important in the assessment of natural attenuation potential at contaminated sites. The hydrogen concentration in groundwater may form a convenient and accurate redox parameter and may give insight into the in situ electron donor activity, which is important for intrinsic dechlorination.

Hydrogen as convenient and accurate redox parameter

Hydrogen measurements in groundwater have proven to provide a more consistent insight into the in situ redox conditions at contaminated sites as compared to traditional methods as redox potential (Eh) measurements with electrodes and the evaluation of the concentrations of macro chemical species in groundwater. Hydrogen measurements can be interpreted in two ways: through empirical relations between hydrogen concentration and redox conditions (the empirical method) and by combining with macro chemical data and thermodynamic calculations (the so-called partial equilibrium approach).

The partial equilibrium approach is the most elaborate method and gives the most complete insight into the redox processes that potentially can occur at the site. This method also does not depend on site specific criteria. Hence, it can serve as a reference to which the results of other methods can be compared. In this project, this was done for the four sites investigated, three chlorinated solvent sites and a landfill site. The redox potential (Eh) measurements were demonstrated to give inconsistent results at three sites. The macro chemical method was inconsistent at two out of four sites tested, including one chlorinated solvent site. Hence, these two traditional methods appear to include a significant risk of erroneous interpretation. The empirical hydrogen method, a relatively simple and straightforward procedure, was demonstrated to give consistent redox results at all three sites contaminated with chlorinated solvents. For the landfill site, the results were inconsistent. The hypothesis is that this deviation was a result of the non-steady-state conditions probably present in the landfill plume.

Hydrogen measurements can become an important new tool in the redox characterisation as part of the stepwise assessment of the natural attenuation potential at contaminated sites. A quick on site scan using the empirical method followed by a more detailed characterisation using the partial equilibrium method appears to be the most appropriate way. The empirical hydrogen method yields consistent redox results at the chlorinated solvent sites tested. Hence, it can serve as a method for an on site quick scan of the redox situation. The costs of this method (200 - 300 EURO per measurement, depending on sample numbers taken per day and per year) are competitive with currently used methods, i.e. standard macro chemical characterisation. In addition, the empirical method has the advantage to yield an immediate impression of the redox situation at the site. The more elaborate method of the partial equilibrium approach, i.e. extending hydrogen measurements with macro chemical analysis and thermodynamic interpretation, can be used to further characterise in more detail. Especially in redox transition zones, this extensive method gives a more complete picture.

Additional research could further improve the hydrogen based redox characterisation. The results of the partial equilibrium approach seem to be very promising, but knowledge gaps have to be addressed in order to use the method optimally. Most important is to study the variations in and the parameter-dependency of the threshold Gibbs energy for biologically mediated electron-accepting reactions. Furthermore the energetics of different iron minerals have to be studied more thoroughly.

On most locations, the comparison of hydrogen concentrations to empirically determined ranges can be used as a single method to obtain a first impression of the redox conditions that exist. More research is needed to achieve a range which is applicable to the Dutch situation where temperatures of the groundwater range between 10 °C and 15 °C. For the landfill site, the results of the empirical hydrogen method were inconsistent with the partial equilibrium results. The hypothesis was that this deviation was a result of the non-steady-state conditions probably present in the landfill plume. Thus, redox interpretations in non-steady-state situations (landfills, recently formed contaminated situations) cannot be made. On the other hand, discrepancies between the results of this method and those of the partial equilibrium approach may be indicative for such non-steady-state conditions. In order to test the validity of this assumption additional research is required.

Hydrogen as indicator for the intrinsic dechlorination and in situ electron donor activity

Measuring hydrogen concentrations may also be valuable for evaluating intrinsic dechlorination processes. This can be done in three different ways:

- Applying thermodynamic calculations to evaluate in situ dechlorination reactions. In this project, most Gibbs energies for the dechlorination reactions were found to be strongly negative, which indicates that dechlorination should occur under almost any condition. This finding is inconsistent with the observations in the field. For an appropriate interpretation determination of threshold Gibbs energies that are valid for the biological dechlorination reactions is needed.
- Comparison of the degree of dechlorination with the hydrogen concentration, in order to determine a range of hydrogen concentrations for which dechlorination is considered optimally. In this project, indications were found that a significant intrinsic dechlorination occurred at sample points where the hydrogen concentrations exceeded a value of 2 nM.
- Correlation between hydrogen concentration and diluted organic carbon concentration (DOC) or co-contaminant concentrations (BTEX, DCA) were found in several data sets obtained at the various test sites. Hence, hydrogen may also be used as an indicator for the in situ electron donor activity. These relations and their relevance for in situ dechlorination should be further explored

From the above it becomes clear that the three methods could not be fully applied in this project, since several knowledge gaps first have to be resolved. Future research should be focused on:

- determination of *threshold* Gibbs energies that are valid for the biological dechlorination reactions;
- identification of optimal hydrogen range for dechlorination processes for conditions typical for the Dutch subsurface and other situations;
- determination of the relation between types of natural carbon sources and their hydrogen release characteristics.

Hydrogen and enhanced natural remediation

The project performed here primarily addressed hydrogen measurements in the context of assessment of natural attenuation. Hydrogen can be considered to be also an important parameter in monitoring enhanced attenuation. The major advantage of such a monitoring is that hydrogen is a very sensitive lump sum parameter responding immediately to changes in redox conditions, making it an effective on site monitoring tool. Introducing more reducing conditions (i.e. when infiltrating electron donor into a chlorinated solvent site) leads to an elevation of hydrogen concentration, and hydrogen can be used to monitor the effect and penetration of the electron donor in the subsurface. On the other hand, introducing more oxidised conditions (i.e. by adding nitrate or oxygen at a BTEX or mineral oil contaminated site), will result in a decrease in the hydrogen concentration. Hence, hydrogen can be used to monitor the performance of an oxida-

tion zone. For the enhanced reductive dechlorination, hydrogen controlled supply of electron donor is probably crucial for an effective remediation. Hydrogen can be controlled by using the appropriate substrate and by using the suitable supply method. Which natural and man-made organics are most suitable as electron donors for intrinsic and enhanced bioremediation is still insufficiently clear. Laboratory and field experiments, some of which are already performed or in preparation, will bring hydrogen based in situ bioremediation again important steps further.

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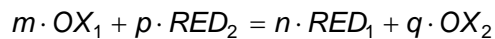
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APPENDIX A

TERMODYNAMIC CALCULATIONS

The energy micro-organisms gain from dechlorination and redox reactions can be calculated thermodynamically as Gibbs (free) energies. By calculating the Gibbs energy for each reaction, terminal electron accepting processes can be classified as energetically favourable or as energetically unfavourable.

Recall the general form of the redox or dechlorination reaction from section 2.1:



The Gibbs energy which is associated with this reaction is calculated in the following way:

$$\Delta G_r = \Delta G^0 + RT \ln \frac{[RED_1]^n \cdot [OX_2]^q}{[OX_1]^m \cdot [RED_2]^p}$$

Where ΔG_r is the Gibbs energy of the reaction, ΔG^0 the Gibbs term at standard temperature, R the gas constant, T the temperature, and between [] the concentrations of the species. For natural redox reactions, such Gibbs equations are listed in the next table. ΔG^0 is calculated from the Gibbs energies of formation of the individual species, which are listed for relevant species (see thermodynamic facts):

$$\Delta G^0 = \sum \Delta G_f^0(\text{products}) - \sum \Delta G_f^0(\text{substrates})$$

Since ΔG^0 is temperature dependent, a correction must be made. This is done by the Van't Hoff equation in the form:

$$\Delta G^{0T_2} = \frac{\Delta H^0(T_1 - T_2) + T_2 \Delta G^{0T_1}}{T_1}$$

Where, ΔH^0 is the enthalpy of the reaction, and T_1 and T_2 the standard and actual temperature, respectively. Since hydrogen is the electron donor of primary interest, the Gibbs energies of reactions have to be calculated per mol hydrogen. Apart from the concentrations of reactants and products, also the in situ conditions (pH and temperature) influence the Gibbs energy of the reactions. The calculated Gibbs energy is thus not a constant value for the entire system, but rather a parameter that applies to one single reaction under specific conditions. Of particular concern in Gibbs energy calculations for iron and manganese reducing reactions is the existence of several different types of iron and manganese oxides. Each of these oxides have a different reactivity and Gibbs energy of formation. It is therefore essential to consider differences in mineralogy and if possible, make a entire characterisation of the oxides involved.

On basis of the calculated Gibbs energy, terminal electron accepting processes are classified as favourable if the calculated Gibbs energy is lower than a threshold value and considered unfavourable if exceeding this value. For redox and dechlorination reactions, this value is between -5 kJ/mol and -20 kJ/mol. The origin of this value is discussed in section 2.2.2.

A second application of thermodynamics is to calculate the minimum hydrogen concentrations, which are required for dechlorination and redox reactions to occur. For each terminal electron process this minimum hydrogen concentration can be calculated with use of the Gibbs energy equation. The minimum hydrogen concentration corresponds to the calculated hydrogen concentration when the Gibbs energy is at the critical value. In the general form of the Gibbs energy equation, the term RED_2 corresponds to the hydrogen concentration:

$$\Delta G_r = \Delta G^0 + RT \ln \frac{[RED_1]^n \cdot [OX_2]^q}{[OX_1]^m \cdot [H_2]^p}$$

In another form it becomes:

$$\Delta G_r = \Delta G^0 + RT \ln \frac{[RED_1]^n \cdot [OX_2]^q}{[OX_1]^m} + RT \ln \frac{1}{[H_2]^p}$$

Where, ΔG_r is between -5 kJ/mol and -20 kJ/mol and ΔG^0 , R , T , RED_1 , OX_1 and OX_2 are known parameters. The minimum hydrogen concentration is the only remaining variable and can thus be calculated. This extrapolation of hydrogen ranges is only validated in situations where hydrogen concentrations are negligible compared to the concentrations of the other components. In these situations the second term in the Gibbs equation is expected to remain constant. Commonly, the hydrogen concentrations in natural environments are in the nM range and the concentrations of other species several factors higher. Therefore it is expected that such low hydrogen concentrations do not affect the concentrations of the other species, and that the second term remains constant. The concentration H^+ , though will be in the same range as hydrogen, but is expected to be buffered. It is important to realise that the calculated minimum hydrogen concentration, associated with a terminal electron accepting process, apply to one particular situation with unique concentrations and conditions. The calculated minimum hydrogen concentrations must therefore not be generalised.

Gibbs equations for important redox and dechlorination reactions

Oxygen reduction	$\Delta G_r = \Delta G^0 + RT \ln \frac{1}{[O_2][H_2]^2}$
Nitrate reduction (I)	$\Delta G_r = \Delta G^0 + RT \ln \frac{1}{[NO_3]^2[H_2]^5[H^+]^2}$
Nitrate reduction (II)	$\Delta G_r = \Delta G^0 + RT \ln \frac{[NO_2^-]}{[NO_3^-][H_2]}$
Nitrate reduction (III)	$\Delta G_r = \Delta G^0 + RT \ln \frac{[NH_4^+]}{[NO_3^-][H_2]^4[H^+]^2}$
Manganese oxide reduction	$\Delta G_r = \Delta G^0 + RT \ln \frac{[Mn^{2+}]}{[H_2][H^+]^2}$
Iron hydroxide reduction	$\Delta G_r = \Delta G^0 + RT \ln \frac{[Fe^{2+}]^2}{[H_2][H^+]^4}$
Sulfate reduction	$\Delta G_r = \Delta G^0 + RT \ln \frac{[HS]}{[H][SO_4^{2-}]}$

Thermodynamic facts

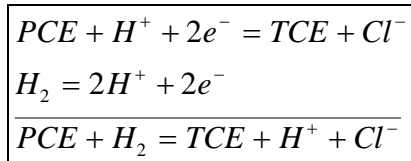
Thermodynamic calculations are based on the Gibbs energy of formation and enthalpy of formation. These data are shown for the relevant species. Values are in kJ/mol and apply to the specie in solution (unless noted else).

	specie	ΔG_f^0	ΔH_f^0
	O ₂	16.32	-11.71
	H ₂	17.57	-4.18
	H ⁺	0	0
liquid	H ₂ O	-237.18	-285.83
	NO ³⁻	-111.3	-207.3
gas	N ₂	0	0
	NH ⁴⁺	-79.37	-132.5
	NO ²⁻	-37.2	-104.6
pyrolusite	MnO ₂	-465.1	-520
	Mn ²⁺	-228	-220.7
goethite	FeOOH	-489	-559.3
amorphous	FeOOH	-452	
siderite	FeCO ₃	-666.7	-737
pyrrhotite	FeS	-100.4	-100
	Fe ²⁺	-78.87	-89.1
	SO ₄ ²⁻	-744.6	-909.2
	H ₂ S	-27.87	-39.75
	HS ⁻	12.05	-17.6
	HCO ³⁻	-586.8	-692
	CH ₄	-34.39	-89.04
	CO ₂	-394.37	-393.5
	Cl ⁻	-131.3	-167.2
	H ₂	17.57	-4.18
	PCE	27.59	-12.43
	TCE	25.41	-19.1
	cDCE	27.8	4.27
	VC	59.65	29
	ethene	81.43	52.47
	ethane	-17.43	-83.85

Source: Stumm and Morgan, 1981
 Dolfing and Janssen, 1994
<http://webbook.nist.gov>

Example of a thermodynamic calculation

The redox reaction in which PCE is dechlorinated with H₂ as electron donor becomes:



In this example the following specie concentrations are assumed:

- [PCE] = 2 · 10⁻⁴ M
- [TCE] = 10⁻⁴ M
- [H₂] = 10⁻⁹ M
- [Cl⁻] = 10⁻³ M

And the following conditions:

- pH = 7 ([H⁺] = 10⁻⁷ M)
- T = 298.15 K (25 °C)

The following constants and values were used:

- R = 8.31451 J/mol
- ΔG_f⁰ (PCE) = 27.6 kJ/mol
- ΔG_f⁰ (TCE) = 25.5 kJ/mol
- ΔG_f⁰ (H₂) = 17.8 kJ/mol
- ΔG_f⁰ (H⁺) = 0 kJ/mol
- ΔG_f⁰ (Cl⁻) = -131.3 kJ/mol

(The ΔG_f⁰ values all apply to the aqueous phase at 298.15 K)

From this information it is now possible to calculate the energy which is involved in the redox reaction mentioned above.

$$\begin{aligned} \Delta G_r &= \Delta G^0 + RT \ln \frac{[TCE] \cdot [H^+] \cdot [Cl^-]}{[PCE] \cdot [H_2]} \\ \Delta G_r &= [\Delta G_f^0(TCE) + \Delta G_f^0(H^+) + \Delta G_f^0(Cl^-)] - [\Delta G_f^0(PCE) + \Delta G_f^0(H_2)] + \\ &RT \ln \frac{[TCE] \cdot [H^+] \cdot [Cl^-]}{[PCE] \cdot [H_2]} \\ \Delta G_r &= (25.5 + 0 - 131.3) - (27.6 + 17.8) + RT \ln \frac{10^{-4} \cdot 10^{-7} \cdot 10^{-3}}{2 \cdot 10^{-4} \cdot 10^{-9}} = -158.6 \text{ kJ / mol} \end{aligned}$$

APPENDIX B

ANALYTICAL RESULTS

Chapter 8: Rademarkt, Groningen.

well	depth (m)	T (°C)	pH	Ec (µS/cm)	Eh (mV)	O ₂ (mg/l)	H ₂ (nM)
demo	6.00 - 7.00	12.3	6.70	2060	4	0.28	0.36
B2	5.65 - 6.65	13.0	6.70	1525	32	0.88	0.29
G2	5.95 - 6.95	13.9					0.18
259	4.60 - 5.60	12.5	7.00	1800	140	0.25	0.49
404	5.00 - 7.00	12.3	6.90	1820	-134		0.37
244	8.10 - 9.10	11.8	7.00	1777	140	0.25	0.17
403	5.00 - 7.00	11.9	7.10	1802	90	0.29	0.11
304	4.00 - 5.00	12.7					0.17
401	5.00 - 7.00	13.6	6.90	2080	-109	0.27	0.12
247	4.90 - 5.90	13.7	7.10	1718	-122	0.14	7.29
303	5.00 - 7.00	13.7	6.80	3130	44	0.18	0.09
215	7.50 - 8.50	13.0	7.00	1920	135	0.11	0.14

well	NO ₃ -N (mg/l)	SO ₄ ²⁻ (mg/l)	Cl ⁻ (mg/l)	TOT-S (mg/l)	DOC (mg/l)	H ₂ CO ₃ (mg/l)	Fe(II) (mg/l)
demo	< 0.04	140	300		13	640	0.21
B2	< 0.04	75	170		12	660	0.1
G2	4.8	73	160		9.8	640	< 0.05
259	< 0.04	170	180		18	720	10
404	< 0.04	0.39	150	< 0.10	21	1200	11
244	6.7	58	290	< 0.10	8.7	490	< 0.05
403	8.3	41	370		8.8	400	< 0.05
304	< 0.04	7.5	260		15	860	4.7
401	1.65	180	250		13	910	3.8
247	< 0.04	1.3	160	< 0.10	18	1000	7.4
303	6.3	150	520		7.3	910	< 0.05
215	0.76	89	280		11	610	< 0.05

well	methane (µg/l)	ethane (µg/l)	ethene (µg/l)	VC (µg/l)	cis-DCE (µg/l)	TCE (µg/l)	PCE (µg/l)
demo	61.1	1.3	0.0	17.1	2655.6	1999.3	2414.8
B2	18.6	2.1	0.0	5.5	520.5	167.3	166.2
G2	3.8	0.2	0.0	0.9	161.6	57.5	276.4
259	150.4	0.1	0.0	0.0	0.0	5.5	6.8
404	5989.9	1.5	0.6	0.0	0.0	4.8	13.2
244	4.4	0.1	1.0	1.1	109.8	146.9	1990.4
403	65.2	0.0	0.0	0.0	23.6	5.1	9.8
304	1239.1	6.8	0.0	0.0	0.0	3.3	5.0
401	276.0	0.3	0.0	0.0	19.6	4.7	4.8
247	14.4	1.2	9.6	0.0	0.0	4.3	2.7
303	124.8	0.0	0.0	0.0	37.2	8.7	15.4
215	107.1	0.8	0.2	4.3	1226.1	681.2	1213.7

Chapter 9: DAF, Eindhoven.

well	depth (m)	T (°C)	pH	Ec (μ S/cm)	Eh (mV)	O ₂ (mg/l)	H ₂ (nM)
NOB5-1	6 - 7	14	7		66	2.8	0.46
C4-2	6.2 - 7.2	14	6		-60	2.8	0.23
C40-1	5.8 - 6.8	14	8		164	0	4.77
C40-2	9 - 10	15	7.8		-177	0	1.09
C47-2	7 - 8	14	6.4		-107	1	0.49
NOB2-1	6 - 7	14	3.8		-94	0	3.07
NOB3-1	6 - 7	13	6.7		0.2	2.5	0.3
C33-1	6 - 7	14	6.5		-150	0	0.2
NOB1-1	6 - 7	14	6.9		-167	1.3	0.8
C32-1	6 - 7	14	6.7		-130	1.3	0.18
B12	6.4 - 7.4	14	6.8		-133	2.8	0.4
C47-3	16 - 17	14	6.4		-170	6.4	0.5
C46-2	13 - 14	15	7.2				0.29
NOB2-2	14 - 15	15	6.4		-132	1.5	4.92
NOB3-2	14 - 15	13	6.9		-183	4.5	0.29
C45-3	14 - 15	14	4.4		-141	0.3	0.46
C27-2	15 - 16	14	6.9		-99	3.4	0.13
C33-2	14 - 15	14	7		-155	2.5	0.1
C39-2	15 - 16	14	6.4		-121	2.6	0.23
C41-1	14 - 15	14	6.9		-167	4.4	0.11
NOB4-2	14 - 15	13	6.3		-100	0.2	0.53
C4-3	14.2 - 15.2	14	7		-80	4.1	0.63
C32-2	14 - 15	14	6.9		-80	0	0.25
C48-3	14 - 15		7.3		-105	0	0.44
B12	14 - 15	14	6.7		-139	1.5	0.13
C51-3	14 - 15	14	6.5		-50	1.3	1.01
C47-4	29 - 30	14	6.7		-166	1.2	0.54
NOB2-3	29 - 30	15	6.6		-120	0.2	1.15
NOB3-3	29 - 30	13	7.3		-198	3.8	2.49
C27-3	28 - 30	14	6.7		-130	1.5	0.27
NOB1-3	29 - 30	16	6.8		-165	1.3	0.4
C41-2	29 - 30	14	7.1		-176	4	0.25
C48-4	29 - 30		6.5				4.25
NOB4-3	29 - 30	13	6.6				0.66
C61	44 - 45	15	6.2		-45	0	1.3
C61	63.5 - 64.5	15	6.9		-120	0	0.58

Chapter 9: DAF, Eindhoven.

well	NO ₃ N (mg/l)	SO ₄ ²⁻ (mg/l)	Cl ⁻ (mg/l)	NO ₂ ⁻ (mg/l)	DOC (mg/l)	HCO ₃ (mg/l)	Fe(II) (mg/l)
NOB5-1	0.2	350	56	0.2		5	0.3
C4-2	0.2	22	14	0.2			1.8
C40-1	0.2	98	220	0.2		390	28
C40-2	0.2	97	230	0.2		210	14
C47-2	0.2	120	56	0.2		59	0.5
NOB2-1	0.3	52	490	0.2		190	19
NOB3-1	0.2	33	60	0.2			0.3
C33-1	0.2	81	210	0.2		69	0.3
NOB1-1	0.2	140	10	0.2		46	0.3
C32-1							
B12	0.2	14	38	0.2		23	0.3
C47-3	0.2	21	190	0.2		22	2
C46-2	0.2	86	250	0.2		180	23
NOB2-2	0.2	40	48	0.2		45	0.3
NOB3-2	0.2	21	36	0.2			0.6
C45-3	0.2	10	15	0.2		34	1.2
C27-2	0.31	10	40	0.2		22	0.3
C33-2	0.2	16	5.2	0.2		5	0.4
C39-2	0.2	53	170	0.2		65	0.3
C41-1	0.2	27	56	0.2			0.4
NOB4-2	0.2	22	14	0.2			1.8
C4-3							
C32-2							
C48-3							
B12	0.2	13	44	0.2		13	0.3
C51-3	0.2	28	14	0.2			1.4
C47-4	0.2	11	23	0.2		5	0.7
NOB2-3	0.2	80	180	0.2		110	7.5
NOB3-3	0.2	13	21	0.2			0.3
C27-3	0.3	34	32	0.2		61	0.7
NOB1-3	0.2	18	21	0.2		5	1.9
C41-2	0.2	13	47	0.2			0.3
C48-4							
NOB4-3							
C61	0.2	660	16	0.2			1
C61	0.2	30	10	0.2			0.3

Chapter 9: DAF, Eindhoven.

well	methane (µg/l)	ethane (µg/l)	ethene (µg/l)	VC (µg/l)	cis-DCE (µg/l)	TCE (µg/l)	PCE (µg/l)
NOB5-1	25	0.25	0.25	0.5	2.5	0.6	0.2
C4-2	100	0.46	1.2	0.5	1	0.2	0.2
C40-1	89	6.3	70	1200	340000	2900	33
C40-2	610	1.3	1.9	310	67000	540	25
C47-2	38	0.25	0.59	4.4	5.6	0.2	0.2
NOB2-1	320	800	0.79	19	29	0.7	0.2
NOB3-1	25	0.25	0.25	0.5	1	0.2	0.2
C33-1	420	3.8	10	52	3500	5700	90
NOB1-1	25	0.25	0.47	2.6	7.9	4.3	0.2
C32-1	250	22	1000				
B12	410	0.25	0.25	0.5	1	0.2	0.2
C47-3	3300	27	420	5200	43000	82	4.7
C46-2	340	0.85	68	56	76	0.5	0.2
NOB2-2	25	0.25	0.25	0.5	1	0.2	0.2
NOB3-2	1600	0.25	0.25	0.5	1	0.2	0.2
C45-3	13000	5.8	0.25	9.2	63	110	5.6
C27-2	25	0.25	0.25	0.5	1	0.2	0.2
C33-2	450	0.25	0.25	0.5	1	0.2	0.2
C39-2	520	0.44	81	780	460	1.8	0.2
C41-1	25	0.25	0.25	0.5	1	0.2	0.2
NOB4-2	16000	0.28	0.25	0.5	1	0.2	0.2
C4-3	< 25	0.25	0.25				
C32-2	45	0.25	15				
C48-3							
B12	210	0.25	0.25	0.5	2.3	1.3	0.2
C51-3	8400	0.25	0.25	0.5	1	0.7	0.2
C47-4	860	0.25	0.25	10	14	0.2	0.2
NOB2-3	540	1.9	93	1200	5500	81	0.2
NOB3-3	780	0.25	0.25	0.5	1	0.2	0.2
C27-3	25	0.25	2.8	55	100	70	140
NOB1-3	2400	0.25	0.6	5.2	4.6	0.2	0.2
C41-2	2500	0.25	0.25	0.5	1	0.2	0.2
C48-4							
NOB4-3	11000	0.25	0.25				
C61	12000	0.96	0.25	2.3	9.2	0.2	0.2
C61	25	0.25	0.25	0.5	1	0.2	0.2

Chapter 10: SBNS, Tilburg.

well	depth (m)	T (°C)	pH	Ec (µS/cm)	Eh (mV)	O ₂ (mg/l)	H ₂ (nM)
156-2	5.5	11.5	5.8		40		0.28
251b	6	12.4	6.2		185		0.42
907	6	12.2	6.7		- 50	0.2	2.14
103	6	15.0	6.8		- 75	0.1	0.31
904	6.5	17.1	5.8		- 18	0.1	0.37
902-2	5 - 6	13.5	6.4		310		0.31
905	5 - 6	12.1	6.3		312		0.16
107	5 - 6	12.5	6.4		148		0.59
902-1	10 - 11	14.3	6.6		307		0.15
A12-2	11	14.0	6.0		229		
A13-2	9 - 11	13.1	6.1		181		0.25

well	NO ₃ ⁻ (mg/l)	SO ₄ ²⁻ (mg/l)	Cl ⁻ (mg/l)	Mn-tot (mg/l)	DOC (mg/l)	HCO ₃ ⁻ (mg/l)	Fe(II) (mg/l)
156-2	0	1.6	34	0.16			0.25
251b	5.6	5.6					
907	0.08	0.17	75	2			
103	0	0.1	160	1.1			17
904	11.6	6.7	47	0.32			0.85
902-2	7.2	3.7	27.3	0	0	0	
905	1.8	9.3	3				

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well	depth (m)	T (°C)	pH	EC (μ S/cm)	Eh (mV)	O ₂ (mg/l)	H ₂ (nM)
BP10F1		9	5.93				2.9
BP10F2		9	5.15				8.3
BP10F3		9	5.58				12.3
BP9F1		9	6.51				0.4
BP9F2		9	6.56				0.4
BP9F3		9	6.09				1.6
BP8F1		9	6.25				2.2
BP8F2		9	6.25				15.6
BP8F3		9	6.25				19.2
BP1F1		9	6.28				23.2
BP1F2		9	6.23				20.2
BP1F3		9	6.10				3.6
BP2F1		9	5.92				1.0
BP2F2		9	6.13				1.0
BP3F1		9	5.78				0.5
BP3F2		9	6.04				0.6
BP3F3		9	6.00				17.9
BP4F1		9	5.20				0.4
BP4F2		9	6.03				0.5
BP5F1		9	5.07				0.3
BP5F2		9	5.96				29.9
BP5F3		9	6.43				24.1
BP6F1		9	5.50				7.2
BP6F2		9	6.15				1.2
BP7F1		9	4.65				3.1
BP7F2		9	5.85				0.3
BP7F3		9	6.20				1.9
BP10F1		9	5.55				21.3
BP10F2		9	6.02				16.1

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well	NO ₃ N (mg/l)	SO ₄ ²⁻ (mg/l)	Mn (mg/l)	NO ₂ ⁻ (mg/l)	NH ₄ (mg/l)	Alk-lab (mmol)	Fe(II) (mg/l)
BP10F1	370.5	43	0	0.1	0.1	0.9	0.3
BP10F2	46.2	108	0.4	0.2	0.6	0.3	15.5
BP10F3	0	138	0.4	0	0.3	0.3	8.9
BP9F1	0	7	0.5	0.2	323.2	48.9	0.3
BP9F2	0	7	0.4	0.3	346.3	56.2	0.1
BP9F3	0	92	0.8	0.1	3	12.2	26.2
BP8F1	0	13	0.8	0.2	410	52.2	50.1
BP8F2	0	32	1.2	0.2	308.3	44.7	55.9
BP8F3	0	22	1.4	0.1	138.3	29.1	76.7
BP1F1	0	6	1	0.2	253.6	36.2	51.4
BP1F2	0	11	1.2	0.1	197.5	33	73.3
BP1F3	0	7	0.5	0	0.9	3.8	6.6
BP2F1	19.7	58	0.4	0.2	73.7	11.5	14.7
BP2F2	0	16	1.1	0.1	206.4	30.1	83.1
BP3F1	17	45	0.4	0.2	77.5	10.1	4.3
BP3F2	0	25	1.3	0.1	124.4	22.1	90.2
BP3F3	0	23	0.7	0	0.7	5.5	16.2
BP4F1	0.1	66	0.3	0.1	1.7	0.7	0.2
BP4F2	0.1	53	1.8	0.1	30.6	19.4	116.3
BP5F1	0.2	157	0.4	0.2	4.4	0.7	1.9
BP5F2	0.1	77	0.6	0.1	111.7	16	61.3
BP5F3	0.1	58	0.3	0.1	0.8	2.6	5.5
BP6F1	0.1	119	0.3	0.1	0.3	0.7	0.1
BP6F2	0.1	9	1	0.1	114.1	19.7	77
BP7F1	0.1	62	0.1	0.1	0.9	0.4	0.2
BP7F2	0.1	7	1.1	0.1	41.2	14.1	76.5
BP7F3	0.1	65	0.2	0.1	0.3	0.5	2.6
BP10F1	0	134	0.6	0	0.5	0.1	26.4
BP10F2	0.1	53	0.3	0.1	0.4	1.2	7.5

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well	methane (mg/l)	ethane (µg/l)	ethene (µg/l)	VC (µg/l)	cis-DCE (µg/l)	TCE (µg/l)	PCE (µg/l)
BP10F1							
BP10F2							
BP10F3							
BP9F1	21.36						
BP9F2	23.64						
BP9F3	8.50						
BP8F1	17.81						
BP8F2	23.4						
BP8F3	20.16						
BP1F1	23.38						
BP1F2	19.14						
BP1F3	1.82						
BP2F1	10.61						
BP2F2	20.88						
BP3F1	8.69						
BP3F2	15.35						
BP3F3	0.02						
BP4F1	5.84						
BP4F2	12.53						
BP5F1	0.42						
BP5F2	12.34						
BP5F3	0.53						
BP6F1	0.74						
BP6F2	17.38						
BP7F1	3.58						
BP7F2	12.27						
BP7F3	0.53						
BP10F1							
BP10F2							