

# HYDROGEN AS INDICATOR FOR REDOX CONDITIONS AND DECHLORINATION

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## Summary

The use of intrinsic degradation processes (natural attenuation) is becoming the basis for the restoration of many contaminated sites. Within this context, measuring concentrations of hydrogen in groundwater is important in two ways. Firstly, the hydrogen concentration can be used to characterize redox conditions. Secondly, hydrogen may be an indicator for the occurrence of dechlorination processes. 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 geochemical parameters were also determined here. Based on these parameters, different methods for data interpretation were applied and compared.

Redox characterisation using hydrogen measurements proved to be a (cost) efficient method to identify the redox condition at the investigated sites, including chlorinated solvent sites. Hydrogen measurements can be used in the following ways:

- a quick on-site scan of the redox situation can be performed by comparing hydrogen concentrations to an empirically determined range; the so-called *empirical hydrogen range*.
- a detailed redox characterisation can be obtained by *the partial equilibrium approach*, which is based on thermodynamic calculations of hydrogen concentrations in combination with concentrations of redox species.

At all investigated sites a consistent characterisation of the redox conditions could be deduced from hydrogen measurements. In contrast, the use of redox potentials and/or macro chemistry alone, would have led to an inconsistent redox characterisation at the investigated sites.

Hydrogen has also been shown to be an indicator for the occurrence of dechlorination processes. Hydrogen concentrations above 2 nM correlated with a high degree of *in-situ* dechlorination. 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 also observed.

## 1 Introduction

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. 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.

### 1.1 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.

### 1.2 Workplan

The following parts have been performed:

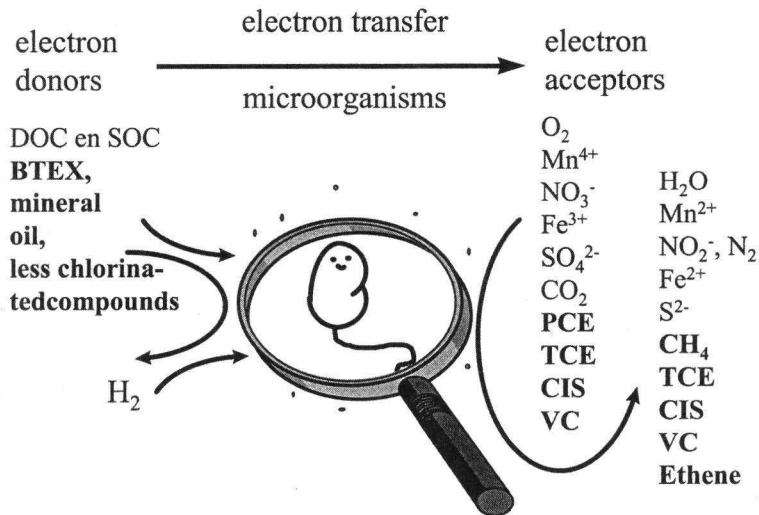
1. development and evaluation of a fundamental scientific knowledge basis for the interpretation of hydrogen measurements for redox characterisation and natural degradation potentials.
2. installation of equipment for analysis and sampling and development of a method for on-site sampling and analyses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

The work was reported in detail in Ter Meer et al (1999).

## 2 Development of scientific knowledge basis for the interpretation of hydrogen measurements

In this part 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

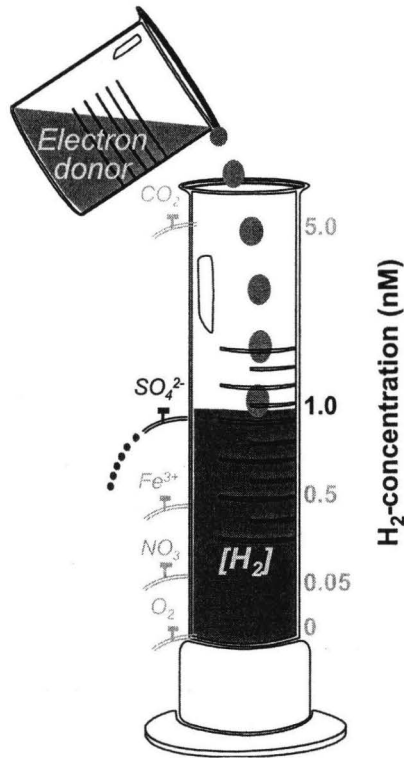
catalysed by microorganisms. Hydrogen is an intermediate in the natural fermentation of organic material in the subsurface. The formed hydrogen interacts with help of microorganisms with other soil and groundwater constituents. Hydrogen is an electron donor, and therefore transfers electrons to electron acceptors. These can be natural electron acceptors like oxygen, nitrate, iron(III), sulphate, en carbondioxide, or pollutants like PCE, TCE and other chlorinated compounds that are dechlorinated through this process (fig.1).



**Fig. 1.** Role of hydrogen and microorganisms in the subsurface redox processes

The concentration level of hydrogen in ground water is determined by a complex network of interrelated processes in which hydrogen is produced out of organic matter and consumed by reactions with electron acceptors. The production of hydrogen from organic matter is a relatively slow process compared to the consumption of hydrogen by electron accepting microorganisms. Therefore hydrogen concentrations are generally very low (nM scale). Microorganisms consume hydrogen to a level in which the reaction just remains feasible. The reason that microorganisms act in this way is competition. Other (groups of) microorganisms that mediate in energetically less favourable electron accepting processes are not able live on these low hydrogen levels.

In Fig. 2 a simplification of the same complex interaction of electron donating en accepting processes is shown.



**Fig. 2.** Schematic representation of the processes which determine the hydrogen concentration

Basically, two different situations can exist:

- the situation of partial equilibrium, and
- the situation far out of equilibrium.

In natural non-disturbed soil systems, processes are often close to equilibrium (partial equilibrium), which means that the production of hydrogen from electron donor sources balances the consumption of hydrogen by electron accepting processes. In Fig. 2 the situation for sulphate reduction is depicted. Oxygen, nitrate and tri-valent iron are absent and sulphate is energetically the most favourable electron acceptor. The sulphate reducing microorganisms consume the hydrogen to a level (1 nM) which is too low for the competing methanogenic microorganisms. As long as the availability of electron donor and sulphate remains, the hydrogen concentration will remain at this level. If all sulphate has been reduced, hydrogen concentrations increase to the level which is favourable for methanogenic microorganisms.

In the situation far out of equilibrium, the electron donor flux is (temporarily) much larger than the electron accepting flux. This will lead to an increased hydrogen concentration, which is no longer a reflection of one particular redox

process. Instead, more electron accepting processes can take place simultaneously. Such situations occur for example at locations where a large contamination of hydrocarbons is present or at landfills. In both cases there will be a large influx of electron donor.

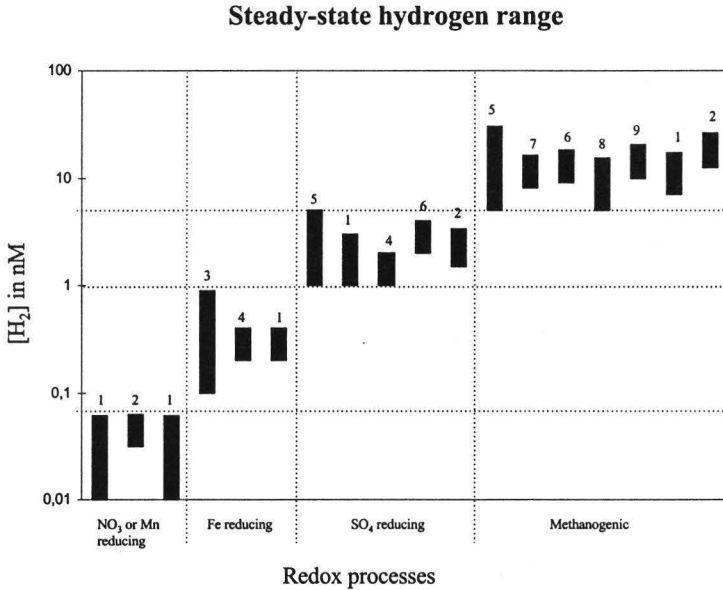
### 3 Methods

#### 3.1 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 ground water 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 "gas-bulb" 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 200 Euro 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.

#### 3.2 Redox identification methods based on hydrogen

For environments that are in partial equilibrium, numerous laboratory studies have been reported in literature, in which *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 (Fig. 3).



**Fig. 3.** overview of steady-state H<sub>2</sub>-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) Vrobleski and Chapelle 1994; (6) Lovley et al. 1982; (7) Lovley and Klung 1982; (8) Goodwin et al. 1988; (9) Conrad et al. 1987

In situations that are far out of equilibrium, empirical hydrogen ranges can not be applied, since they do not reflect particular redox processes. The measured values of hydrogen can also be interpreted by combined use of hydrogen concentrations and macro chemical parameters in a *thermodynamic calculation* (also referred to as the partial equilibrium approach). This approach is able to establish whether or not redox processes are favourable, i.e. can occur at that certain sampling point. The advantage of the thermodynamic approach is that it is independent of site specific criteria. By calculating the Gibbs energy, a particular redox reaction can be considered as thermodynamic favourable or unfavourable depending whether or not the value is below or above the threshold Gibbsenergy. The threshold Gibbs energy is the minimum amount of energy that microorganisms need in order to carry out the reaction and 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.

## 4 Field research

In this research the performance of four redox identification methods have been applied and mutually compared:

- *redox-potential* determination (de 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 (de empirical method),
- and interpretation of *hydrogen measurements* with thermodynamic calculations on the basis of hydrogen concentrations en macro chemical parameters (the thermodynamic method).

Furthermore from the concentrations of chlorinated hydrocarbons and degradation products the degree of dechlorination was deduced and compared to redox characteristics and other parameters like DOC-content and the presence of co-contaminants like BTEX.

In total four different sites have been investigated. The results are summarized below.

*Redox characterisation.* The usefulness of hydrogen measurements for redox characterisation is depicted in the following table (see Tab. 1). 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 macro chemistry or redox potential measurements. The empirical method appears to be a very useful instrument for a first screening of the redox situation at a site. After this a more detailed sampling and analysis program can be conducted in which hydrogen concentrations and macro chemistry are determined and then can be interpreted with thermodynamic calculations, thus leading to a more complete and adequate redox picture.

**Tab. 1.** 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 and macro chemistry)
Groningen	-	+	+	++
Eindhoven	+/-	-	+	++
Tilburg	+/-	+	+	(*)
Boxtel	(**)	-	-	++

- 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

*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 level 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. Additional field and laboratory research is currently performed and further supports that hydrogen threshold values above which reductive dechlorination becomes possible exist. Preliminary results indicate threshold values between 1 and 2 nM which are depending on the degree of dechlorination of the compound.

## 5 Conclusions and recommendations

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. Additionally, a more thorough redox characterisation can be conducted following a more focused sampling and analyses program 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. 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 ( $> 2\text{-}3\text{ nM}$ ) and high degrees of dechlorination. Possibly, the hydrogen concentration needs to exceed a certain threshold value 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 microorganisms was identified as an hypothesis to be tested. Current field and laboratory research confirms the existence of such thresholds.

## References

- Chapelle, F.H. and Lovley, D.R., 1992. Competitive exclusion of sulfate reduction by Fe(III)-reducing bacteria: a mechanism for producing discrete zones of high-iron groundwater. *Groundwater*, 30: 29-36
- Conrad, R., Lupton, F.S. and Zeikus, J.G., 1987. Hydrogen metabolism and sulfate-dependent inhibition of methanogenesis in a eutrophic lake sediment (Lake Mendota). *FEMS microbiological ecology*, 45: 107-115
- Goodwin, S., Conrad, R. and Zeikus, J.G., 1988. Relation of pH and microbial hydrogen metabolism in diverse sedimentary eco-systems. *Applications of environmental microbiology*, 54: 590-593
- Hoehler, T.M., Alperin, M.J., Albert, D.B. and Martens, C.S., 1998. Thermodynamic control on hydrogen concentrations in anoxic sediments. *Geochimica et cosmochimica acta*, 62(10): 1745-1756
- Lovley, D.R., Dwyer, D.F. and Klung, M.J., 1982. Kinetic analysis of competition between sulphate reducers and methanogens for hydrogen in sediments. *Applications of environmental microbiology*, 43: 1373-1379
- Lovley, D.R. and Goodwin, S., 1988. Hydrogen concentrations as an indicator of the predominant terminal electron-accepting reactions in aquatic sediments. *Geochimica et cosmochimica acta*, 52: 2993-3003
- Lovley, D.R. and Klung, M.J., 1982. Intermediary metabolism of organic matter in the sediments of a eutrophic lake. *Applications of environmental microbiology*, 43: 552-560.
- Lovley, D.R. and Philips, E.J.P., 1987. Competitive mechanisms for the inhibition of sulfate reduction and methane production in the zone of ferric iron reduction in sediments. *Applications of environmental microbiology*, 53: 2636-2641
- Ter Meer, J., Gerritse, J., di Mauro, C., Harkes, M.P. and Rijnaarts, H.H.M., 1999. Hydrogen as indicator for in situ redox condition and dechlorination. CUR/NOBIS report 96.024
- Vrobletsky, D.A. and Chapelle, F.H., 1994. Temporal and spatial changes of terminal electron-accepting processes in a petroleum hydrocarbon-contaminated aquifer and the significance for contaminant biodegradation. *Water resources research*, 30: 1561-1570