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## Optimization of the Sampling Technique for the Determination of Dissolved Hydrogen in Groundwater

In this study a field-sampling technique for dissolved hydrogen ( $H_2$ ) in groundwater will be presented which allows the transport of gaseous samples into the laboratory for further analysis. The method consists of transferring the headspace trapped in a gas-sampling bulb which is continuously purged by groundwater into previously evacuated vials using a gas-tight syringe. Three transfer steps with preceding evacuation of the vial led to a  $H_2$ -recovery of 100% in laboratory experiments. The method has been applied to determine  $H_2$  concentrations in an aquifer contaminated with chlorinated solvents.

Tests concerning the effect of different pumping techniques on  $H_2$  concentrations revealed that most reliable values were obtained with a bladder pump, while an electrically driven submersible pump generated considerable amounts of hydrogen due to electrochemical interactions with the sampled water. Concentrations of dissolved hydrogen in field and laboratory samples were about two orders of magnitude higher when sampling was performed with the electrically driven submersible pump compared to sampling with the bladder pump and a peristaltic pump.

Lab experiments with a Plexiglas reservoir to produce  $H_2$ -enriched water were used to study the effect of two tubing materials (PVC, polyamide) on  $H_2$  losses. PVC tubing turned out to allow transfer of  $H_2$ -enriched water over 25 m without significant losses, while PA-tubing was not suitable for sampling of  $H_2$ .

### Optimierung der Beprobungstechnik für gelösten Wasserstoff in Grundwasser

In dieser Studie wird eine Beprobungstechnik für gelösten Wasserstoff ( $H_2$ ) in Grundwasser vorgestellt, die den Transport gasförmiger Proben ins Labor zur Analytik ermöglicht. Die Methode besteht aus dem Transfer der Gasphase in einer von Grundwasser durchflossenen Gasmaus in evakuierte Vials mit Hilfe einer gasdichten Spritze. Drei Transfer-Schritte mit jeweils vorhergehender Evakuierung des Vials führten in Labor-experimenten zu einer  $H_2$ -Wiederfindung von 100%. Diese Methode wurde angewendet, um  $H_2$ -Konzentrationen in einem mit chlorierten Lösungsmitteln kontaminierten Grundwasserleiter zu bestimmen.

Versuche zum Effekt verschiedener Pumptechniken auf die  $H_2$ -Konzentration zeigten, dass die verlässlichsten Daten mit einer Membranpumpe erhalten wurden, während eine elektrisch betriebene Tauchmotorpumpe durch elektrochemische Wechselwirkungen mit dem beprobten Wasser beträchtliche Mengen an Wasserstoff erzeugte.

Konzentrationen von gelöstem Wasserstoff waren in Feld- und Laborproben etwa zwei Größenordnungen höher, wenn die Probenahme mit der elektrisch betriebenen Tauchmotorpumpe durchgeführt wurde – verglichen mit einer Probenahme durch die Membranpumpe oder eine peristaltische Pumpe.

Laborexperimente mit einem Plexiglas-Reservoir, in dem ein künstlich mit  $H_2$  angereichertes Wasser hergestellt werden konnte, wurden durchgeführt, um den Effekt zweier Schlauchmaterialien (PVC, Polyamid) auf Verluste von  $H_2$  zu studieren. PVC-Schlauchmaterial mit einer Länge von 25 m erwies sich als geeignet für den Transfer von  $H_2$ -angereichertem Wasser, während PA-Schlauchmaterial sich als nicht geeignet für eine  $H_2$ -Probenahme zeigte.

**Keywords:** Redox Characterization, Pumping Technique, Tubing Material, Bubble-strip Method, MP1, Gaseous Sample

**Schlagwörter:** Redoxcharakterisierung, Pumptechnik, Schlauchmaterial, Gasblasen-Strip-Methode, MP1, Gasförmige Probe

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Research Paper

## 1 Introduction

Characterization of redox conditions is not a straightforward procedure and no reliable method exists to unambiguously predict the fate of a certain compound in a solution with respect to the nature and the concentration of the bulk electron donors and acceptors [1]. This is especially the case for redox voltages measured with a platinum electrode due to the lack of internal equilibrium [2], the occurrence of mixed potentials [3], and non-electroactive behavior of the elements O, H, N, C, and oxidized S [4].

As was emphasized by Chapelle et al. [5],  $H_2$  concentrations in anaerobic systems can be interpreted in the context of electron-acceptor (oxygen, sulfate, nitrate) availability and the presence of reduction products (Fe(II), sulfide, methane) and is therefore a useful additional parameter to deduce the prevailing anaerobic metabolic activity. Terminal electron-accepting processes (TEAP) yield different Gibbs free energies ( $\Delta G_r$ ) for the oxidation of a given electron donor, e.g.,  $H_2$ . Accordingly, the steady-state concentration of hydrogen in sediments will follow the order: methanogenic > sulfate-reducing > Fe(III)-reducing > Mn(IV)-reducing > nitrate-reducing, as the potential energy yield from  $H_2$  oxidation increases [6]. This concept was applied to a shallow groundwater system contaminated with solvents and jet fuel [5]. Measurements of redox voltages and the concentrations of hydrogen were made to delineate the zonation of redox processes. Redox voltages indicated that Fe(III)-reduction was the predominant redox process in the anaerobic zone and did not indicate the presence of methanogenesis or sulfate reduction. In contrast, measurements of  $H_2$  concentrations indicated that methanogenesis predominated in heavily contaminated sediments near the water table ( $H_2 \approx 7 \text{ nmol L}^{-1}$ ) and that the methanogenic zone was surrounded by distinct sulfate-reducing ( $H_2 \approx 1\text{--}4 \text{ nmol L}^{-1}$ ) and Fe(III)-reducing zones ( $H_2 \approx 0.1\text{--}0.8 \text{ nmol L}^{-1}$ ). These results were confirmed by the distribution of dissolved oxygen, sulfate, Fe(II), and methane in the groundwater.

Practical considerations to measure hydrogen in groundwater are made by Chapelle et al. [7] and Bjerg et al. [8]. Details like pumping technique, tubing or well-casing material are decisive for the accuracy of the  $H_2$  determination. Considering that loss of hydrogen may occur during sampling and measurement in the laboratory, development of a reliable sampling technique is strongly required.

Sampling of  $H_2$  is typically performed using the bubble-strip method developed by Chapelle and McMahon [9]. In this method, a gas-sampling bulb is purged by groundwater at a low flow-rate of about 300–600 mL  $\text{min}^{-1}$ . About 25 mL of  $N_2$  gas is then injected into the bulb via a septum. The resulting headspace is equilibrating with groundwater which is continuously passing for about 30 min. Analysis of  $H_2$  is then

performed directly in the field using a gas chromatograph with a reduction gas detector (RGD). However, application of this method in a routine measurement protocol, e. g., in the context of natural attenuation studies, is disadvantageous due to the need of portable gas chromatography instrumentation. So far, no method to transport and store samples for a time frame of days has been reported.

In this study we will report a sampling technique which allows the transport of gas samples into the laboratory for further analysis. The method is based on the bubble-strip method described above, however, it avoids the field-analysis step. Rather, a technique is described which allows the transport of gaseous samples into the laboratory after transfer of part of the headspace trapped in the gas-sampling bulb into glass vials. This procedure was used to quantify the effect of different pumping techniques on  $H_2$  concentrations in samples taken from an aquifer contaminated with chlorinated solvents.

## 2 Material and methods

### 2.1 Laboratory experiments

#### 2.1.1 Transfer of $H_2$ -standards into glass vials

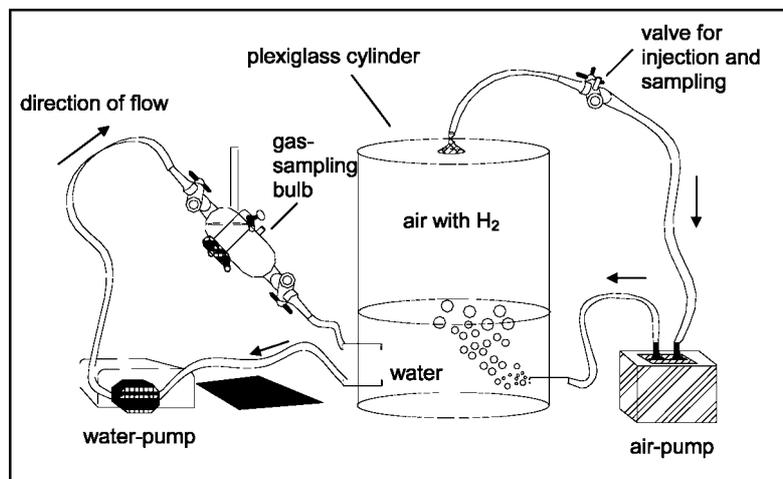
In order to sample groundwater for dissolved hydrogen without using a field gas-chromatograph, a technique was tested that allows transferring  $H_2$ -standards into evacuated 5 mL glass vials (Fisher Scientific), ready for transport and storage, by use of a 10 mL gas-tight pressure-lock syringe (SGE).

All glass vials were sealed with a PTFE-coated butyl rubber stopper and an aluminum crimp cap (both VWR). They were then evacuated via the septum by use of a vacuum pump (MZ 2c, Vacuubrand).

A volume between 5 mL and 10 mL of a  $H_2$ -standard could now be transferred into the glass vial.  $H_2$  concentrations of the standard and the glass vial could then be analyzed and compared for recovery. This procedure was repeated several times to study the effect of several transfer steps with subsequent evacuation on the recovery of the  $H_2$ -standard.

#### 2.1.2 Test of sample set-up with a reservoir of $H_2$ -enriched water

A set-up was created to produce water with a defined  $H_2$  concentration. This water was produced in a gas-tight reservoir and could be sampled with the material also used in the field (i.e. tubing, gas-sampling bulb, septa). The bladder



**Fig. 1:** Experimental set-up for testing field-sampling equipment for the bubble-strip method.

Versuchsaufbau zum Testen der Probenahme-Ausrüstung für die Gasblasen-Strip-Methode.

pump and the electrically driven pump could not be tested with this set-up due to the limited size of the reservoir (8 L). The set-up developed by McInnes and Kampbell [10] served as a model for this construction.

The reservoir consisted of a Plexiglas cylinder with a volume of 8 L (Fig. 1). This cylinder was filled with 1.5 L deionized water and closed gastight. Two circulation systems were then produced within the reservoir – one for the gas phase and one for the water phase. A Miniport gas pump (50 Hz, KNF) was used to suck air from the upper part of the reservoir and re-inject it at the lower end at a rate of approximately  $3.3 \text{ L min}^{-1}$  producing gas-bubbles within the water column.

A peristaltic pump (Multifix) allowed water circulation within the reservoir and also sampling with the bubble-strip method outside the reservoir. The flow-rate was about  $250 \text{ mL min}^{-1}$ .

Via a valve sealed with a rubber-septum a defined volume of pure H<sub>2</sub> gas could be injected into the gaseous circulation system. This volume was between 250  $\mu\text{L}$  and 1 mL in all experiments.

After 3 h of equilibration of the two phases the sampling procedure of the bubble-strip method was started. The H<sub>2</sub> concentration within the N<sub>2</sub>-bubble in the gas-sampling bulb was analyzed every 10 min and compared with the concentrations in the gas phase of the reservoir analyzed directly before the start of the sampling procedure and directly afterwards.

Using this set-up it was possible to determine the time the sampling procedure takes for equilibration. Also, it was possible to incorporate different tubing materials into the circu-

lation thereby testing their suitability for sampling of dissolved hydrogen.

### 2.1.3 H<sub>2</sub> concentration of tap water sampled with different pumping techniques

In order to study possible effects of different pumping techniques on the concentration of dissolved hydrogen, lab experiments with different pumps sampling tap water were conducted. Tap water (pH = 8.05,  $EC_{25} = 280\text{--}310 \mu\text{S cm}^{-1}$ , O<sub>2</sub>-saturation = 110%,  $\vartheta = 19.8^\circ\text{C}$ ) was chosen rather than deionized water in order to simulate a pristine, aerobic natural water.

A 1.7 m long PVC-pipe ( $\varnothing 12.7 \text{ cm}$ ) was filled with fresh tap water. This water was then sampled with three different pumps according to the bubble-strip method [9]: A bladder pump (UIT), an electrically driven submersible pump (MP1, Grundfos) and a peristaltic pump (Multifix).

In order to get an impression of the effect of ion strength on the H<sub>2</sub> concentration measured with the electrically driven submersible pump the specific conductivity of the tap water was increased to about  $1 \text{ mS cm}^{-1}$  by the addition of NaCl in an additional experiment.

Furthermore, an experiment was conducted in which two pumps were placed into the pipe: the electrically driven pump above the bladder pump. Water was pumped with the electrically driven pump and re-injected at the lower end of the pipe in close vicinity to the bladder pump. This water was then sampled for H<sub>2</sub> with the bladder pump. Thus, water coming from the electrically driven pump could not only be sampled by this pump itself but by an additional, independent pump in order to get supplementary information on the content of dissolved hydrogen.

For each experiment the pipe was emptied and re-filled with fresh tap water. The pipe was open to atmosphere in all experiments.

## 2.2 Field sampling

Field samples were taken from a triassic sandstone aquifer at a landfill site near Kronach in Northeast Bavaria, Germany. Some 50 years ago acidic sludge from oil reprocessing was deposited there on an area of about 400 m<sup>2</sup> resulting in a groundwater contamination of petroleum hydrocarbons and chlorinated solvents along with sulfuric acid. Field samples were taken in September and October 2002 at one well upstream the landfill and at five sampling points downstream.

### 2.2.1 Pumping techniques

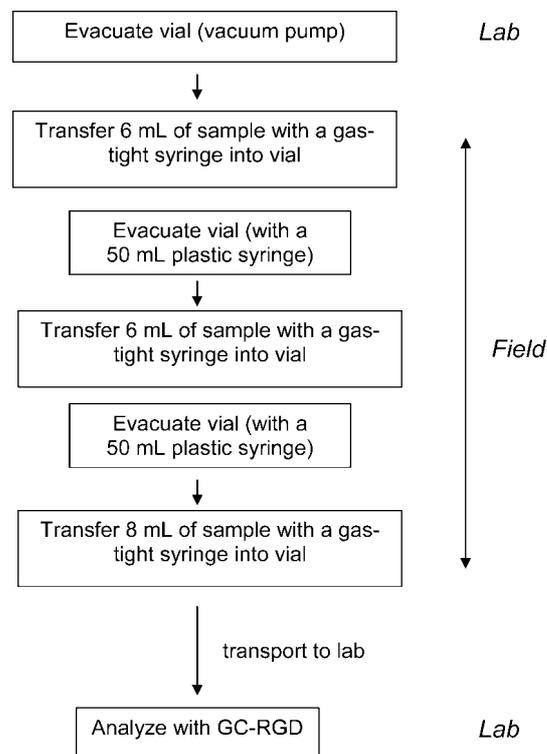
Two different pumps were used to study their effect on hydrogen concentrations in the field and in the lab: The first pump is a bladder pump, consisting of a stainless-steel casing with a bladder inside which can be inflated thereby forcing water upward by exerting a positive pressure. Flow-rates with this pump were between 250 mL min<sup>-1</sup> and 300 mL min<sup>-1</sup>. The second pump used in this study was an electrically driven submersible pump powered by a field generator. With this pump flow-rates of up to 0.7 L s<sup>-1</sup> can be achieved. During dissolved hydrogen sampling a flow-rate similar to that of the bladder pump was applied. Additionally, a peristaltic pump was used for lab experiments. Flow-rates with this pump were between 250 mL min<sup>-1</sup> and 300 mL min<sup>-1</sup>.

### 2.2.2 Sampling and analysis of dissolved hydrogen (H<sub>2</sub>)

Each well was purged prior to sampling until standard parameters like pH, specific conductivity, oxygen saturation, and redox potential remained constant.

Sampling for dissolved hydrogen was performed using the bubble-strip method described by Chapelle and McMahon [9]. A 125 mL gas-sampling bulb (2-2146-U, Supelco) with glass stopcocks at each end was purged by groundwater at a rate of about 270 mL min<sup>-1</sup>. 25 mL N<sub>2</sub> gas were then injected via a septum (Half-Hole Thermogreen, Supelco). Water was pumped at the same rate for 45 min allowing the N<sub>2</sub>-bubble to reach equilibrium with the water flowing past it.

After equilibration of both phases 6 mL of the N<sub>2</sub>-bubble were withdrawn as described above for the transfer of H<sub>2</sub>-standards (Par. 2.1.1). The evacuation was performed in the laboratory prior to the sampling day. After injection of the sample aliquot, the glass vial was evacuated again – this



**Fig. 2:** Sampling scheme for transfer of H<sub>2</sub>-sample into 5 mL glass vials.

Probenahme-Schema für den Transfer einer H<sub>2</sub>-Probe in 5 mL-Glasvials.

time in the field using a 50 mL plastic syringe (Omnifix, Braun). This procedure was then repeated once more. Finally, 8 mL of the N<sub>2</sub>-bubble were withdrawn and injected into the glass vial creating an overpressure on the order of 150...300 hPa. The glass vial was then transported cool and dark to the laboratory where it was analyzed within the next two days. This scheme is visualized in Figure 2.

Hydrogen gas was separated from other gaseous compounds with a gas chromatograph equipped with a molecular-sieve column (5 Å, 1.5 m × 2 mm, WTW). Helium was the carrier gas, injector and column were operated at ambient temperature. H<sub>2</sub> was detected by a reduction gas detector (Trace Analytical).

## 2.3 Calculation of H<sub>2</sub> concentrations

Calibration is performed using standards with different volume fractions  $\varphi$  of H<sub>2</sub> in the gas phase (usually expressed as ppm):

$$\varphi(\text{H}_2) = \frac{V(\text{H}_2)}{V_{\text{tot}}} \quad (1)$$

$V(\text{H}_2)$ : volume of H<sub>2</sub>  
 $V_{\text{tot}}$ : total gas volume

The concentration of pure H<sub>2</sub> gas at atmospheric pressure can be derived using the ideal gas law, which yields  $c(\text{H}_2) = 40.9 \text{ nmol L}^{-1}$  at  $\vartheta = 25^\circ\text{C}$  and  $p = 1013.25 \text{ hPa}$ . Consequently, a gas mixture with a volume fraction for H<sub>2</sub> of  $\varphi = 10^{-6}$  (= 1 ppm) corresponds to a H<sub>2</sub> concentration in the gas phase of  $40.9 \text{ nmol L}^{-1}$ , which can be converted into a water-phase concentration of H<sub>2</sub> using the dimensionless Henry's law constant, which is  $K_{\text{H}} = 52.3$  at  $25^\circ\text{C}$  [11]:

$$c_{\text{aq}} = \frac{40.9 \text{ nmol L}^{-1}}{52.3} = 0.78 \text{ nmol L}^{-1} \quad (2)$$

$c_{\text{aq}}$ : H<sub>2</sub> concentration in the aqueous phase (unit: nmol L<sup>-1</sup>)

All calculations were performed for actual water temperature interpolating between values obtained from Wilhelm et al. [11], which are given in  $5^\circ\text{C}$  increments.

A linear relationship between volume fraction and peak heights in GC-RGD was observed over a range of 0.3...110.4 ppm.

### 3 Results and discussion

#### 3.1 Laboratory experiments

##### 3.1.1 Transfer of H<sub>2</sub>-sample into glass vials

The results for the transfer of H<sub>2</sub>-standards into evacuated vials by use of gas-tight syringes are shown in Table 1. In this table the recovery has been calculated from the H<sub>2</sub> con-

**Table 1:** Recovery of H<sub>2</sub>-standards transferred into glass vials via gas-tight syringes.

Wiederfindung von H<sub>2</sub>-Standards, die mit gasdichten Spritzen in Glasvials überführt wurden.

Number of transfer steps	Recovery
1	90.8% (± 1.4%)
2	95.9% (± 0.5%)
3	100.0% (± 0.6%)

centration of the standard before the start of the experiment and the H<sub>2</sub> concentration in the glass vials after each transfer step.

The transferred volumes were 7 mL for one and two transfer steps and  $2 \times 5 \text{ mL}$  and  $1 \times 8 \text{ mL}$  (in this order) for three transfer steps. H<sub>2</sub> volume fractions of standards used in these experiments were between 4.1 ppm and 52.4 ppm.

It can be observed that one and two transfer steps with preceding evacuation of the glass vial do not lead to a complete recovery of the standard ( $n = 7$  and  $n = 5$ , respectively). Only when three transfer steps were performed an average recovery of 100.0% (± 0.6%,  $n = 6$ ) could be achieved.

This is due to the fact that complete vacuum can not be achieved with standard laboratory and field equipment. Therefore, each evacuation procedure leaves a certain amount of molecules inside of the vial. By performing several transfer steps with evacuation between each step the composition of these molecules becomes increasingly similar to that of the sample transferred into the vial. This leads to an increasing recovery with each step approaching 100% after three steps.

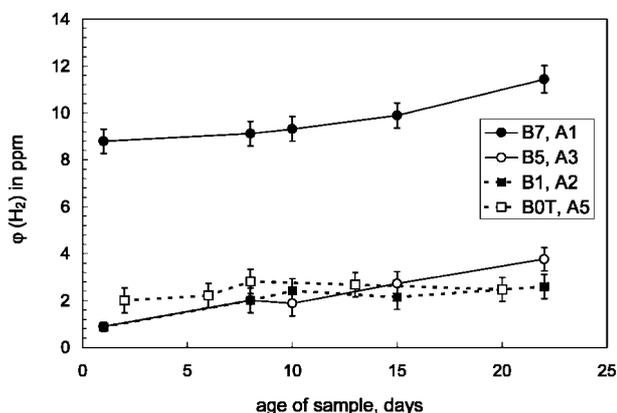
#### 3.1.2 Stability of gaseous standards and samples containing H<sub>2</sub>

##### 3.1.2.1 Standards

H<sub>2</sub>-standards produced and stored in 120 mL glass bottles which were sealed with the same technique and material used for field samples (PTFE-coated butyl rubber stopper secured by an aluminum crimp cap) were stable over several days. Volume fractions of a 49.5 ppm standard were about 98.1% after six days ( $n = 2$ ). As the standards were produced to have a slight positive pressure of about +155 hPa the pressure loss via the septum over time can also be used as an indicator of stability of this sealing method. After seven days H<sub>2</sub>-standards of about 5 ppm had a pressure of 102% (± 1.0%,  $n = 9$ ) compared to the week before. These results suggest that the sealing method used in this study is suitable for storing gaseous samples for at least 2...3 days prior to analysis.

##### 3.1.2.2 Samples

The development of H<sub>2</sub> concentrations of four gaseous field samples (trapped in 5 mL glass vials) was observed over time. All samples were analyzed 1 or 2 days after sampling. After that, they were stored at ambient temperature and daylight conditions for 6 and 8 days, respectively, and analyzed



**Fig. 3:** H<sub>2</sub> volume fractions of four gaseous field samples stored for a period of 20...22 days; all samples stored at ambient temperatures and daylight starting on day 0, samples B1 and B0T stored dark and cool (4 °C) starting on day 6 and 8, respectively.

H<sub>2</sub>-Volumenanteile von vier gasförmigen Feld-Proben, die für eine Dauer von 20...22 Tage gelagert wurden; alle Proben wurden von Tag 0 an bei Raumtemperatur und Tageslicht gelagert, Proben B1 und B0T wurden von Tag 6 bzw. Tag 8 an bei Dunkelheit und kühl (4 °C) gelagert.

again. Then, 2 out of 4 samples (B1 and B0T) were stored dark and cool (at 4 °C), whereas the other two samples were still stored at ambient temperature and daylight conditions. The concentrations were monitored for 20...22 days (Fig. 3).

Surprisingly, no losses of H<sub>2</sub> over time could be observed. On the contrary, concentrations of all samples increased between the first (day 1...2) and the second measurement (6 or 8 days). For samples of well B5 and B7 which have been stored at daylight for the entire period of the experiment this upward trend continues until day 22 (solid lines in Fig. 3). The H<sub>2</sub> volume fraction in the B7 sample increases from 8.8 ppm (day 1) to 9.3 ppm (day 10) and finally 11.4 ppm on day 22.

In contrast to this, the upward trend is slowed down and stopped from day 6...8 in samples from well B1 and B0T which have been stored cool and dark beginning at day 6...8. The H<sub>2</sub> concentration even decreases a little bit, then stabilizing at a level observed near day 8...10.

These results strongly suggest photochemical reactions inside the glass vials as microbial processes seem unlikely to produce such changes of concentration in pure gaseous samples. For this reason samples obtained using this method should be transported and stored dark and cool, and should be analyzed within 1...2 days after sampling.

### 3.1.3 Using a reservoir of H<sub>2</sub>-enriched water for testing field-sampling set-up

In the first experimental set-up H<sub>2</sub>-enriched water was transported from the reservoir to the gas-sampling bulb through a PVC tubing (cf. Fig. 1). In all experiments water was then re-injected into the reservoir also with a PVC tubing (about 0.5 m).

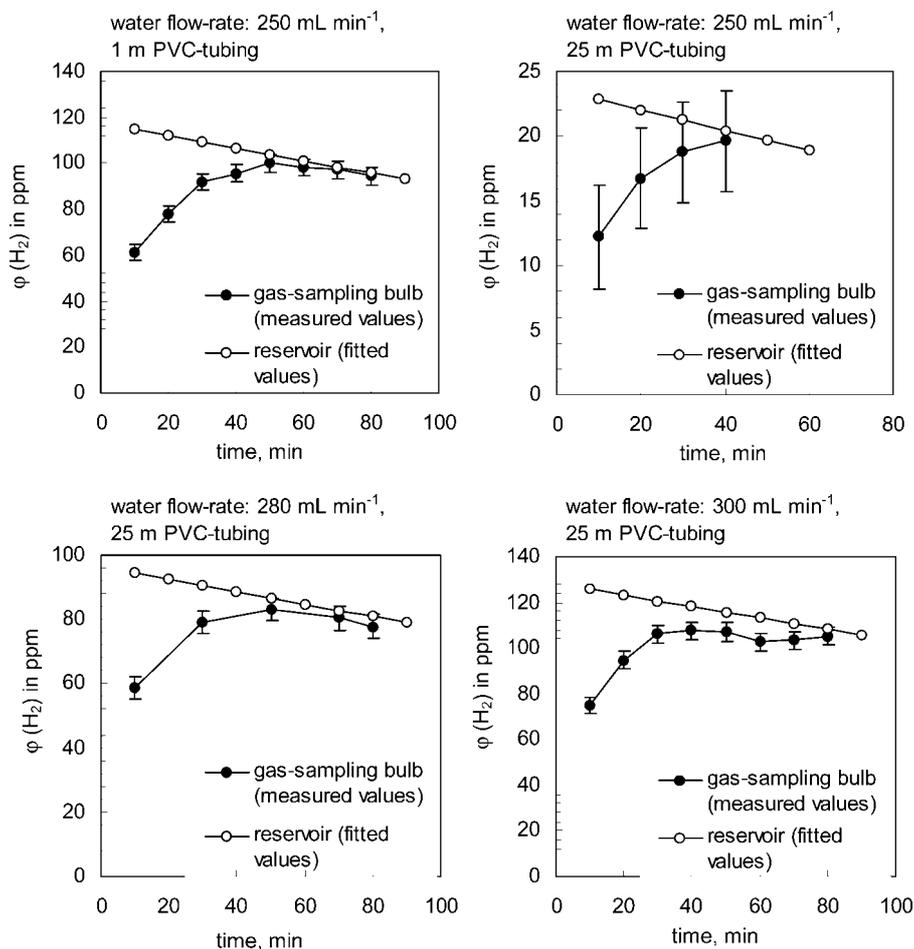
Figure 4 shows the course of H<sub>2</sub> volume fractions in the gas phases of both the gas-sampling bulb and the reservoir, connected by a 1 m PVC tubing and by a 25 m PVC tubing, respectively. The time at  $t = 0$  min corresponds to the time of injection of 25 mL N<sub>2</sub> gas into the gas-sampling bulb.

The H<sub>2</sub> concentration within the headspace of the reservoir was not constant probably due to losses through conjunctions, valves, or tubing. Furthermore, it was not possible to simultaneously monitor H<sub>2</sub> concentrations of both headspaces due to the fact that only one measurement could be performed in 10 min. For these reasons the headspace H<sub>2</sub> concentration in the reservoir was analyzed at  $t = 0$  min and  $t = 90$  min and computed in between using a first-order kinetic function. Error indicators of gas-sampling bulb headspace volume fractions in Figures 4 and 5 represent the interval of prognosis ( $P = 95\%$ ) for a single measurement calculated from the linear calibration.

From Figure 4 it can be seen that equilibrium within the gas-sampling bulb is achieved after about 50 min for both tubing lengths. From there on, the absolute concentration in the gas-sampling bulb decreases also indicating an equilibrium between the gas phases of the two systems.

The 25 m PVC tubing which was also used in field sampling shows hardly any hydrogen losses. For the 250 mL min<sup>-1</sup> flow-rate the concentration measured at  $t = 40$  min corresponds to 96.2% of the fitted concentration at the same time. The values for the other two experiments using a 25 m PVC tubing (flow-rates: 300 mL min<sup>-1</sup> and 280 mL min<sup>-1</sup>) are at 50 min 92.6% and 96.0%, respectively. Given the uncertainty of the fit of the reservoir headspace concentration this a satisfactory recovery.

Additional experiments were conducted with a 50 m PA-tubing which was an accessory for the bladder pump. It consists of double tubing for water and air transport – one pipe for each. The air-pipe is used to inflate the bladder which pushes water upward through the water-pipe. This double-tube was now incorporated into the circulation between reservoir and gas-sampling bulb using the water-pipe for transport of H<sub>2</sub>-enriched water. As in all experiments water was pumped by a peristaltic pump. Therefore, conclusions can only be drawn as to the tubing material of the bladder pump, but not about the bladder pump itself. Figure 5 shows the



**Fig. 4:** Reservoir headspace H<sub>2</sub> volume fractions and gas-sampling bulb H<sub>2</sub> volume fractions using PVC tubing of different length (1 m and 25 m) and different flow-rates.

Reservoir-Gasraum-H<sub>2</sub>-Volumenanteile und Gasraum-H<sub>2</sub>-Volumenanteile bei Benutzung von PVC-Schläuchen verschiedener Länge (1 m und 25 m) und bei verschiedenen Flussraten.

results of these experiments using flow-rates of water between 60 mL min<sup>-1</sup> and 300 mL min<sup>-1</sup>.

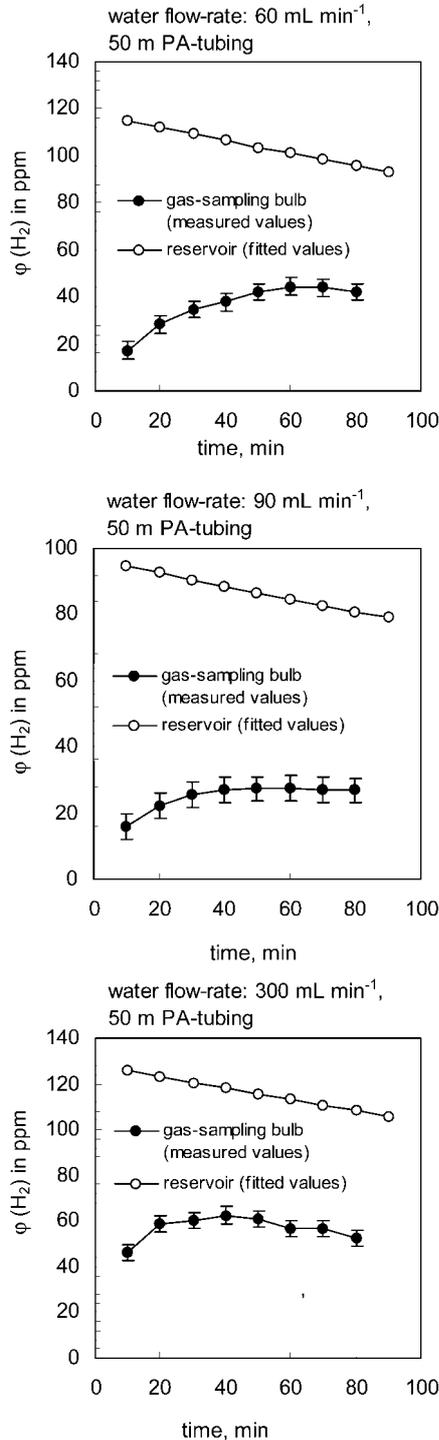
Obviously the equilibrium concentration in the gas-sampling bulb does not correspond to the reservoir headspace concentration. Maximum H<sub>2</sub> concentrations within the headspace of the gas-sampling bulb were observed after 60 min ( $Q = 60$  mL min<sup>-1</sup> and  $Q = 90$  mL min<sup>-1</sup>) and 40 min ( $Q = 300$  mL min<sup>-1</sup>), respectively. From this point concentrations decrease nearly parallel to the concentrations in the headspace of the reservoir. Because there is still such a gap between both headspace concentrations even at the point where gas-bulb headspace concentrations decrease again (after 40 min and 60 min, respectively) significant losses through the tubing material are likely.

At  $t = 80$  min the concentration in the headspace of the gas-sampling bulb corresponded to only 43% ( $Q = 60$  mL min<sup>-1</sup> and  $Q = 90$  mL min<sup>-1</sup>) and 64% ( $Q = 300$  mL min<sup>-1</sup>) of the reservoir headspace concentration. This suggests that the higher flow-rate could compensate for some of the losses on the way through the tubing. But as a flow-rate of about

300 mL min<sup>-1</sup> is the maximum which can be achieved in the field using the bladder pump this is not satisfactory.

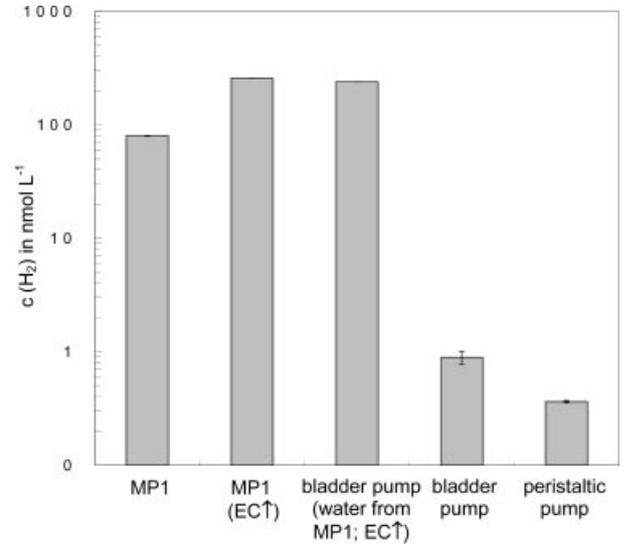
Degassing through tubing material has also been reported by McInnes and Campbell [10], who tested polyethylene and silicon tubing. But in these experiments the loss of H<sub>2</sub> to the atmosphere via the materials used was less than 1% in 30 min. The degree of degassing seems to be dependant on the flow-rate, the length and the material of the tubing. Chapelle et al. [7] even used diffusion of H<sub>2</sub> through teflon-tubing as a passive sampling method. The time for equilibrium in these experiments was approximately 8 hours.

In our case the losses observed using this tubing could not only be due to PA material but to the special set-up of this double-tube with possible losses at the contact between air-tube and water-tube. Also, the longer tubing length compared to the PVC tubing (50 m vs. 25 m) has to be taken into consideration. However, the comparison between a 1 m and 25 m PVC tubing reveals no major losses due to this length difference (Fig. 4). Thus, length variations on this order should not have a major impact on losses of H<sub>2</sub>. There-



**Fig. 5:** Reservoir headspace H<sub>2</sub> volume fractions and gas-sampling bulb H<sub>2</sub> volume fractions using 50 m PA tubing at different flow-rates.

Reservoir-Gasraum-H<sub>2</sub>-Volumenanteile und Gasraum-H<sub>2</sub>-Volumenanteile bei Benutzung eines 50 m-PA-Schlauches bei verschiedenen Flussraten.



**Fig. 6:** H<sub>2</sub> concentration of tap water sampled with different pumps (EC ↑ : artificially increased electric conductivity; see text for details).

H<sub>2</sub>-Konzentration von Leitungswasser, das mit verschiedenen Pumpen beprobt wurde (EC ↑ : künstlich erhöhte elektrische Leitfähigkeit; Details siehe Text).

fore, our results suggest that performing laboratory tests on the sampling set-up that is used in the field can yield important information concerning the suitability of sampling material.

### 3.1.4 Sampling tap water for H<sub>2</sub> with different pumping techniques

The results of the sampling of tap water with different pumps are shown in Figure 6. The first two columns show the H<sub>2</sub> concentration obtained from sampling with the electrically driven submersible pump. The addition of NaCl in order to increase the specific conductivity of the tap water has obviously also increased the H<sub>2</sub> concentration obtained with this pump from 79.9 nmol L<sup>-1</sup> to 256.9 nmol L<sup>-1</sup>. This corroborates the theory that electrochemical reactions with the electrically driven pump create high H<sub>2</sub> concentrations [7] on a qualitative basis. A higher conductivity obviously also enhances the effect of this interaction.

Moreover, the MP1-samples show a H<sub>2</sub> concentration which is more than two orders of magnitude above the ones sampled with the bladder pump alone and the peristaltic pump (notice the logarithmic scale of the diagram). Very similar results have been observed by Chapelle et al. [7] using a direct current (dc) electrically driven submersible

pump. In our study, however, we could show that the type of groundwater pump most frequently used in Germany is not suitable for H<sub>2</sub>-sampling due to these effects (see also Par. 3.2).

Also, water which has been pumped through the MP1 and directed to and sampled with the bladder pump shows high H<sub>2</sub> concentrations. These are similar to the concentrations observed when sampling with the MP1 alone ( $(239.4 \pm 0.6) \text{ nmol L}^{-1}$  vs.  $(256.9 \pm 0.6) \text{ nmol L}^{-1}$ ). This indicates that the lower H<sub>2</sub> concentration measured with the bladder pump alone ( $(0.9 \text{ nM} \pm 0.1) \text{ nmol L}^{-1}$ ) and nearly reproduced with the peristaltic pump ( $(0.4 \pm 0.01) \text{ nmol L}^{-1}$ ) is realistic and not due to possible losses inside the pump (e.g., through the bladder). Obviously, the bladder pump is able to produce realistic results when sampling H<sub>2</sub>-enriched water.

The concentrations measured in the headspace of the gas-sampling bulb in these experiments were assumed to be in equilibrium with water at 20 °C. The electrically driven MP1 increases this initial water temperature. The maximum water temperature observed at the end of an experiment was 40 °C. Therefore, calculations performed for 20 °C slightly overestimate aqueous phase H<sub>2</sub> concentrations as Henry's law constant for H<sub>2</sub> increases with increasing temperatures. A worst-case estimation for the comparison of  $\vartheta = 20 \text{ °C}$  and  $\vartheta = 40 \text{ °C}$  yielded a H<sub>2</sub> concentration of about 91 % of the concentration shown in Figure 6. Thus, this effect does not alter the principal conclusions one can derive from this.

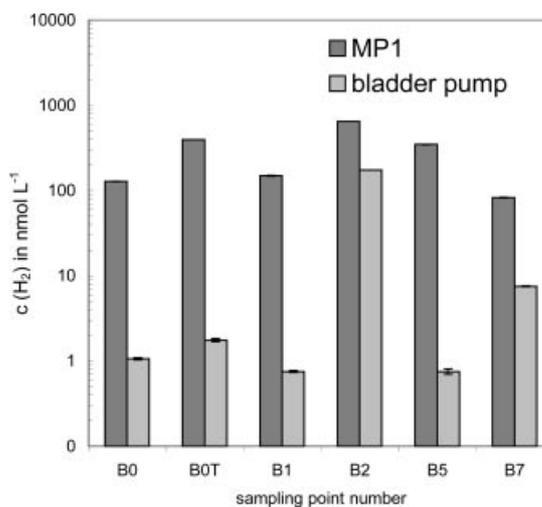
### 3.2 Field samples: Effect of pumping technique on H<sub>2</sub> concentration

The transfer method depicted in Figure 2 was applied successfully in a groundwater contaminated with chlorinated ethenes. Six sampling points at the Kronach site were sampled with the bubble-strip method using two different pumps, first using the MP1-pump, later the bladder pump. All samples were obtained in September and October 2002. At least two weeks lay between sampling of the same well with a different pump in order to avoid interference of both methods. Figure 7 shows a comparison of both methods. Again, a logarithmic scale was chosen for better visualization. Apart from well number B2 H<sub>2</sub> concentrations obtained with the MP1 are about two orders of magnitude higher than H<sub>2</sub> concentrations obtained with the bladder pump.

This, together with the information from lab experiments, clearly demonstrates that the electrically driven pump is not suitable for H<sub>2</sub>-sampling due to electrolytically produced hydrogen.

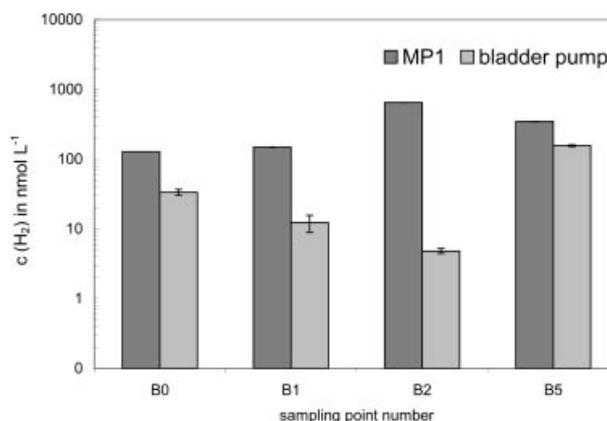
In order to study the degree of interference, both pumping methods were also performed directly after each other at 4

sampling points – starting with the MP1-pump. The results are shown in Figure 8.



**Fig. 7:** Concentration of dissolved hydrogen (H<sub>2</sub>) in six sampling points at the Kronach site using two different pumps.

Konzentration von gelöstem Wasserstoff (H<sub>2</sub>) an sechs Messstellen der Kronacher Untersuchungsfläche bei Benutzung zweier unterschiedlicher Pumpen.



**Fig. 8:** Concentration of dissolved hydrogen (H<sub>2</sub>) in four sampling points at the Kronach site using two different pumps: sampling with bladder pump directly after sampling with MP1.

Konzentration von gelöstem Wasserstoff (H<sub>2</sub>) an vier Messstellen der Kronacher Untersuchungsfläche bei Benutzung zweier unterschiedlicher Pumpen: Probenahme mit der Membranpumpe unmittelbar nach der Probenahme mit der MP1.

Compared with the values shown in Figure 7, H<sub>2</sub> concentrations determined using the bladder pump in sampling points B0, B1, and B5 are about 1...2 orders of magnitude higher when sampling was performed directly after MP1-sampling. In contrast to this, well B2 showed a much lower bladder pump H<sub>2</sub> concentration when sampled directly after MP1-sampling. These results also rule out the possibility of purging a well by use of a MP1-pump prior to H<sub>2</sub>-sampling, even if a different pump is employed in the bubble-strip method.

#### 4 Conclusions

The transfer of gaseous samples into glass vials using a gas-tight pressure-lock syringe seems to be a promising approach for sampling groundwater for dissolved hydrogen. It is an efficient and easy-to-do method compared to the use of a field gas-chromatograph.

Using this method the effect of different pumping techniques on observed H<sub>2</sub> values could be quantified. One important result presented in this study is that an electrically driven submersible pump is not suitable for sampling of dissolved hydrogen in groundwater even at low flow-rates. This is obviously due to electrochemical interactions between this electrically driven pump and the sampled water, and could also be observed in the laboratory sampling tap water. Also, care has to be taken when this pump is used for purging of sampling points prior to the sampling procedure even if the latter is done by another pump.

Moreover, a technique for the production of H<sub>2</sub>-enriched water in the laboratory could be successfully used to test different tubing materials for sampling of dissolved hydrogen. Our results suggest that the sampling set-up used in the field should be tested in the laboratory by this or similar constructions. In our case, this led to the replacement of the default PA-tubing delivered along with a bladder pump by PVC-tubing.

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