Doctoral Thesis

Investigations of gas exchange in quasi-saturated porous media using noble gases as conservative tracers

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Investigations of gas exchange in quasi-saturated porous media using noble gases as conservative tracers

A dissertation submitted to the
SWISS FEDERAL INSTITUTE OF TECHNOLOGY ZURICH
for the degree of
Doctor of Natural Sciences

presented by
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2002
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Abstract

The concentrations of the noble gases He, Ne, Ar, Kr and Xe in groundwater are usually found to exceed their respective atmospheric solubility equilibrium concentrations. Because of its relative elemental composition and – in case of Ne, Ar, Kr and Xe – its atmospheric origin, this ubiquitous supersaturated component has come to be known as “excess air”. Although neither the phenomenon of excess air nor its formation is very well known, it nevertheless has a very important effect on the gas exchange between (soil-) air and the saturated zone. In subsurface hydrology, the presence of excess air crucially affects the quantitative interpretation of studies using trace gases as tracers (e.g., for groundwater dating or the determination of paleorecharge conditions). In addition, since the excess air component initially includes all atmospheric gases, the presence of excess air can result in significantly enhanced concentrations of biochemically relevant gases like oxygen in the saturated zone. Although the composition of the excess air component suggests that its presence is likely to be due to the additional dissolution of atmospheric air, no detailed investigations of its formation have yet been conducted to confirm this hypothesis. Consequently, there is no satisfactory physical explanation for the generation of excess air, so that the excess air phenomenon is still not thoroughly understood.

In this work, a series of laboratory experiments were performed to identify the relevant processes involved in the formation of excess air. These experiments involved the use of dissolved noble gases to trace the origin and composition of excess air.

In quartz sand columns, excess air was generated in a reproducible manner by the dissolution of entrapped air bubbles. Depending on water flow conditions, different elemental patterns of the dissolved gas excess were measured that ranged from a purely atmospheric composition to a fractionated type analogous to that expected based on the closed-system equilibration (CE) concept. This CE approach postulates the equilibration of a finite water volume with a finite air volume under the slightly increased
hydrostatic pressure in the quasi-saturated zone. In the experiments, the amount of dissolved gas in excess is controlled by the hydrostatic pressure and the initially entrapped air volume. The composition of the excess air component is influenced by the water flow regime, by the entrapped air bubble size distribution, by the initial composition of the dissolved gases, and by the initial composition of the entrapped gas phase.

The results of the column experiments were critically examined in an investigation on excess air formation in a large sand filter used in the purification of the drinking water of the city of Zurich, Switzerland. This scaled-up experiment, with much larger temporal and spatial dimensions, yielded results comparable to those from the small-scale column experiments, thus supporting the previous findings.

For a more detailed insight into the evolution of the dissolved gas composition during the process of excess air generation, a kinetic multi-species model for dissolved gas transport in porous media in the presence of entrapped air bubbles was developed. It predicts concentration changes in water and in entrapped gas bubbles resulting from the dissolution of the gas bubbles. The results of the model were found to agree very well with the measured experimental data.

A comprehensive interpretation of the experimental data, together with a numerical analysis of the air bubble dissolution process in porous media, enabled us to develop a physically sound concept for the formation of excess air in quasi-saturated porous media. The generation of excess air under such conditions is coupled to the presence of entrapped air and influenced by the amount of entrapped air, the size distribution of the entrapped air bubbles, the hydrological flow conditions pertaining, the initial dissolved gas composition, and the initial entrapped gas composition.
Zusammenfassung


Zusammenfassung


Chapter 1

Introduction

1.1 Noble gases and excess air

In 1957, Shinya Oana reported on argon and nitrogen measurements made in natural waters. Between 1949 and 1950 he had sampled precipitation, river water, lakes and groundwater in Nagano province, Japan. Astonishingly, all groundwater samples had Ar concentrations that exceeded the expected solubility equilibrium concentrations by up to 39 % (Oana, 1957). Since that time, the supersaturation of atmospheric gases in groundwater is known to be a phenomenon that permanently accompanies hydrologists and geochemists working with naturally dissolved gases. As the composition of the dissolved gas excess is often similar to that of atmospheric air, Heaton and Vogel (1981) introduced the term “excess air” to describe this general supersaturation. Although excess air is a ubiquitous attribute of most groundwaters, only recently has scientific attention been focused on this topic. One major reason for the relatively poor awareness of the excess air phenomenon is the fact that the most “popular” dissolved gas species in groundwater – oxygen – usually shows no evidence of any supersaturation at all, because soil respiration and biochemical oxidation processes mask any signal which might be left by the dissolved oxygen component of excess air.

Since the discovery of the excess air phenomenon in the 1950s, the question of how excess air is formed in groundwater has often been posed, but has never been answered satisfactorily. The atmospheric composition of the excess component suggests that an additional air reservoir is likely to be its source. Oana (1957) therefore proposed the displacement of air pockets from the near-surface soil zone into deeper regions during
the process of infiltration to be the mechanism behind the formation of excess air. In the deeper, usually saturated, soil zone, these air pockets can dissolve under the influence of the higher hydrostatic pressure prevailing there. Until now, all other attempts to explain the generation of excess air in groundwater have been based on this concept of discrete air volumes that can be dissolved in the saturated zone. Nevertheless, a comprehensive investigation of this type of process has never been performed, leaving the problem of how groundwater can be supersaturated with atmospheric gases basically unsolved.

At present, the processes involved in the formation of excess air are not known in detail and there is no appropriate physical description of the excess air phenomenon. The main purpose of this work is therefore to provide a thorough understanding of how excess air is formed and to provide an interpretation of the excess air phenomenon within the general context of the exchange of gases between groundwater and soil air.

To achieve these aims, atmospheric noble gases were used as environmental tracers. In recent years, noble gases have increasingly been employed in subsurface tracer studies. The main objectives of such noble gas studies in groundwater are generally the assessment of groundwater migration and groundwater age (e.g., Schlosser et al., 1988; Castro et al., 1998), the evaluation of paleoclimatic conditions during groundwater recharge (e.g., Andrews and Lee, 1979; Stute et al., 1992a), and the determination of geochemical processes in the shallow crust (e.g.; Ballentine et al., 1991; Stute et al., 1992b). Furthermore, noble gases provide an excellent instrument to study gas transfer between groundwater and soil air. The absence of any kind of non-physical interactions affecting the chemical state of the dissolved noble gases, together with the well-defined inputs for the atmospheric noble gases, make noble gases extremely suitable for the analysis of air/water partitioning in groundwater.

Recent progress in the interpretation of bulk dissolved noble gas patterns in water (Aeschbach-Hertig et al., 2000), together with a newly developed optimization routine that takes into account not only elemental abundance, but also isotopic ratios (Peeters et al., accepted), allow in-depth investigations of air-water mass transfer processes to be conducted.
As a consequence, most of the present work focuses on noble gases and their use to understand how excess air is generated and to explain the composition of dissolved gases in groundwater.

1.2 Outline

This thesis employs two strategies to foster a more detailed understanding of the excess air component. On the one hand, conceptual and physical models are used to interpret and predict the dissolved gas composition in groundwater. These models are presented in Chapter 3 and Chapter 4. The other part of this work summarizes and discusses the experimental investigation of the formation of excess air. Starting with laboratory column experiments in Chapter 5, larger scale experiments under quasi-laboratory conditions (Chapter 6) and a field application of noble gases (Chapter 7) follow. Both aspects of this work – the theoretical modeling and the experimental measurements – are tightly connected. Only with the help of relevant models was a comprehensive interpretation of the measured data able to yield new insights into the formation of excess air and into the dynamics of air/water partitioning in groundwater.

The thesis is structured as follows:

In Chapter 1, the basic principles of gas dissolution in groundwater are discussed in the light of the omnipresent excess air component. The practical relevance of the excess air phenomenon in tracer hydrology and geochemistry is also illustrated in this first chapter.

Chapter 2 gives a short overview of the available bulk concepts of excess air formation. These conceptual models are mainly used in tracer hydrology to explain noble gas patterns commonly encountered in groundwaters. Owing to their rather simple structure, they are not capable of describing the formation of excess air in detail, but they are
nevertheless important tools for the overall interpretation of the dissolved noble gases in groundwater.

In Chapter 3, a newly developed kinetic multi-species model for the dissolution of entrapped air bubbles in water-saturated porous media is presented. In contrast to the bulk excess air concepts, this model allows a detailed study of bubble-mediated gas exchange in groundwater. This chapter has been submitted for publication in *Environmental Science & Technology*.

Chapter 4 outlines the result of laboratory column experiments aimed at studying the process of excess air formation in quasi-saturated porous media. In these experiments, it was possible for the first time under well-defined laboratory conditions to verify the proposed mechanism that explains the formation of excess air in terms of the partial or complete dissolution of entrapped air bubbles. This chapter has been accepted for publication in *Geochimica et Cosmochimica Acta*.

Chapter 5 presents the findings of a scaled-up experiment that verifies the laboratory results on the formation of excess air. A large sand filter in the waterworks of the city of Zurich which had been put back into operation, was monitored over a period of six months. The temporal evolution of the dissolved gas concentrations measured in the filter outflow validates the results from the laboratory column experiments and confirms that the scheme of air/water partitioning in quasi-saturated porous media developed from these experiments can be scaled-up to ‘real world’ dimensions.

Finally, in Chapter 6 the role of excess air in a real-world field study is elucidated. In the Valle di Blenio, Ticino, Switzerland, a combined geochemical and noble gas approach was used to investigate the interaction between groundwater and river water in an ecologically sensitive alpine floodplain. It could be shown that a thorough understanding of the excess air component can be essential for the correct determination of apparent groundwater ages using the $^3$H-$^3$He dating method. This chapter has been published in *Ground Water* (Holocher et al., 2001).
Chapter 2

The excess air component in groundwater

Whenever dissolved noble gases in groundwater are considered, their supersaturation with respect to the atmospheric solubility equilibrium at the given water temperature, salinity, and barometric pressure is evident. Since the composition of the dissolved gas excess often is similar to that of atmospheric air, Heaton and Vogel (1981) introduced the term “excess air” for this common phenomenon. Oana (1957) was the first to report argon supersaturation in groundwater samples from a Japanese aquifer. In the following, the presence of excess air was reported for karstic aquifer systems (Herzberg and Mazor, 1979; Mazor, 1972) and sedimentary aquifers (Andrews and Lee, 1979; Heaton and Vogel, 1979). Today, excess air is known to be present in virtually any kind of natural groundwater system. Consequently, excess air is manifest in tropical aquifers (e. g.; Stute et al., 1995b), in arid zones (e. g.; Heaton and Vogel, 1979) and under temperate climatic conditions (e. g.; Beyerle et al., 1998). It can be found in very old, deep aquifer systems (e. g.; Stute et al., 1995a) as well as in recently infiltrated, near-surface groundwater (e. g.; Beyerle et al., 1999) for a broad lithologic variety ranging between lowly permeable granites and highly permeable alluvial deposits. The most common range of possible hydrogeologic and climatic conditions in which excess air is present emphasizes that this supersaturation of atmospheric gases is a fundamental property of almost all groundwaters.
2.1 Relevance of excess air in subsurface hydrology

If atmospheric trace gases are employed as environmental tracers within the soil–groundwater system, excess air must be taken into account in analyzing and interpreting the data. In applications such as groundwater dating or the determination of recharge conditions, the solubility equilibrium concentration of the considered gaseous tracer usually provides the desired information. If, for example, transient gases like SF\(_6\) are used to calculate groundwater residence times, the apparent water age is defined by the amount of gas that was dissolved in equilibrium with the atmosphere. This implies that the excess air component has to be separated from the total measured concentration in order to determine the required equilibrium fraction (Schlosser et al., 1989; Busenberg and Plummer, 2000). To obtain reliable information, a rigorous physical approach to the separation of the various components is necessary, which requires at least a basic knowledge of the processes involved in the formation of excess air (Aeschbach-Hertig et al., 1999; Ballentine and Hall, 1999). Details on the available approaches that allow the separation of excess air from other components (mainly the solubility equilibrium component) are given in Chapter 3.

A prominent example of the use of atmospheric trace gases in groundwater studies, with the associated separation of excess air component and equilibrium concentrations, is given by the determination and reconstruction of paleorecharge conditions from dissolved noble gas concentrations. According to Henry's law, the amount of dissolved gas in equilibrium with the atmosphere depends on the partial pressure of the gas in the atmosphere, on all other dissolved species — commonly summarized in the bulk parameter salinity — and on the water temperature. Assuming no further gas exchange between water and soil air takes place, the physical soil conditions prevailing at the time of infiltration can be reconstructed from measurements of the dissolved noble gases.
Besides the relevance of excess air for trace gas methods in groundwater, the excess air component itself most probably conveys information about past climatic and recharge conditions and aquifer characteristics. The amount of excess air may be related to the amount of precipitation and the temperature regime (Heaton et al., 1986; Stute and Talma, 1998; Aeschbach-Hertig et al., 2001), and the aquifer lithology (Wilson and McNeill, 1997).

Finally, excess air in groundwater is also important for the biogeochemistry of the transition zone between groundwater and the unsaturated zone. Because excess air – in the meaning of its initial definition – contains all atmospheric gases (i.e., including oxygen and nitrogen), a dissolved oxygen source in the uppermost aquifer zone exists which is usually not taken into account, although it may significantly contribute to the oxygen budget in a groundwater body. Note that in most cases the biogeochemical consumption of oxygen prevents the direct detection of the excess air component in the dissolved oxygen concentrations.

### 2.2 Air dissolution in groundwater

Excess air apparently plays a major role in the exchange of gases between soil air and groundwater. A thorough understanding of air dissolution and the physical processes controlling the air/water partitioning at the groundwater table is therefore of vital importance.

The most important source of noble gases in groundwater is the solution of atmospheric gases according to Henry’s law:

\[
C_i^* = \frac{C_i^a}{K_{H,i}(T,S)} = \frac{p_i}{RT K_{H,i}(T,S)} = \frac{x_i \cdot P}{RT K_{H,i}(T,S)}
\]  

(2.1)
The equilibrium concentration $C^*$ of the dissolved gas $i$ in solution is directly proportional to its atmospheric concentration $C^a$. The molar atmospheric concentration is related to the partial pressure $p_i$ in the gas phase according to Dalton’s Law in which $R$ is the universal gas constant. The concentration proportionality is given by the dimensionless Henry coefficient $K_{H,i}$, which depends on temperature $T$ and salinity $S$. $x_i$ is the mole fraction of gas $i$ in the atmosphere and $P$ is the barometric pressure.

### Table 2.1: Molecular diffusivities and dimensionless Henry coefficients.

<table>
<thead>
<tr>
<th></th>
<th>5 °C</th>
<th>15 °C</th>
<th>25 °C</th>
<th>5 °C</th>
<th>15 °C</th>
<th>25 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$D$</td>
<td></td>
<td></td>
<td>$K_{H}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>[10$^{-5}$ cm$^2$/s]</td>
<td></td>
<td></td>
<td>[(mol/l gas) / (mol/l water)]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>He</td>
<td>5.10</td>
<td>6.30</td>
<td>7.22</td>
<td>107</td>
<td>107</td>
<td>105</td>
</tr>
<tr>
<td>Ne</td>
<td>2.61</td>
<td>3.28</td>
<td>4.16</td>
<td>83.4</td>
<td>88.0</td>
<td>90.7</td>
</tr>
<tr>
<td>Ar</td>
<td>1.63</td>
<td>2.13</td>
<td>2.69</td>
<td>20.9</td>
<td>25.2</td>
<td>29.3</td>
</tr>
<tr>
<td>Kr</td>
<td>1.02</td>
<td>1.41</td>
<td>1.84</td>
<td>10.5</td>
<td>13.4</td>
<td>16.4</td>
</tr>
<tr>
<td>Xe</td>
<td>0.774</td>
<td>1.12</td>
<td>1.47</td>
<td>5.36</td>
<td>7.29</td>
<td>9.41</td>
</tr>
<tr>
<td>N$_2$</td>
<td>1.11</td>
<td>1.49</td>
<td>1.96</td>
<td>46.8</td>
<td>55.6</td>
<td>63.5</td>
</tr>
<tr>
<td>O$_2$</td>
<td>1.36</td>
<td>1.80</td>
<td>2.35</td>
<td>22.9</td>
<td>27.7</td>
<td>32.2</td>
</tr>
</tbody>
</table>

**$D$:** Molecular diffusivities in water. Measured values for He, Ne, Kr and Xe were taken from Jähne et al. (1987). The diffusivity of Ar was approximated by the relationship $D_i \sim 1/(\text{mass})^{0.5}$ using the measured values of He, Ne, Kr and Xe. Diffusivities of oxygen and nitrogen were taken from Broecker and Peng (1974).

**$K_{H}$:** Dimensionless Henry coefficients. They are calculated using the equilibrium concentrations from Weiss (1970), Weiss (1971), Weiss and Kyser (1978) and Benson and Krause (1980) for He, Ne, Ar and Kr, and from Clever (1979) for Xe.

The atomic mass of the noble gases influences their behavior in air–water partitioning. The solubility of the noble gases increases with increasing atomic mass (Tab. 2.1). As a result, in solubility equilibrium with the atmosphere the dissolved gas composition is enriched in the heavy gases relative to atmospheric air. Furthermore, the temperature
dependency of the gas solubility rises with increasing atomic weight. Thus Kr and Xe react most sensitive on the actual water temperature during groundwater recharge whereas He can be considered almost independently from the temperature (Kipfer et al., submitted).

The molecular diffusivity of the noble gases in water decreases with increasing atomic mass (Tab. 2.1). This implies that any diffusive alterations of dissolved noble gas concentrations have the strongest effect on the light noble gases.

![Graph showing supersaturation of noble gases](image)

**Figure 2.1:** Example of a dissolved excess pattern resulting from the complete dissolution of an entrapped air volume in groundwater. The supersaturation is given relative to the atmospheric solubility equilibrium concentrations.

Based on the equilibrium fractionation, the addition of atmospheric air to solubility equilibrium concentrations yields a characteristic supersaturation pattern in which the least soluble light noble gases show the largest excess (Fig. 2.1). The degree of super-
saturation is often given as relative Ne excess ($\Delta Ne$), i.e. the percentage of the Ne excess ($Ne_{excess}$) relative to the Ne equilibrium concentration ($Ne^*$).

$$\Delta Ne\ (%) = \frac{Ne_{excess}}{Ne^*} \cdot 100$$ (2.2)

As Ne reacts only slightly to temperature, $\Delta Ne$ is an almost directly observable quantity that measures the amount of injected excess air.

If we assume that the infiltrated water that enters the groundwater is in equilibrium with the (soil-) atmosphere, three different processes may be responsible for generating a dissolved excess of atmospheric gases:

1. Complete dissolution of an additional air reservoir,
2. Mixing of water components that equilibrated at different temperatures,
3. Changes in the parameters $T$, $S$ and $P$ that define the solubility equilibrium concentration.

In the latter process, an equilibrated water parcel is considered that enters the saturated zone, and hence is isolated from any gas exchange with the atmosphere. With increasing water temperature and salinity, the maximum amount of gas that can dissolve decreases (Tab. 2.2). The amount of gas actually dissolved in the water parcel therefore represents an apparent supersaturation for rising $T$ or $S$ values. As the effects of $T$ and $S$ increase with the molar mass of the gas, the expected resulting excess pattern would favor the heavy gases, which is contrary to the characteristic excess air signal.

Changes in $P$ have an uniform effect for all gases and hence do not change the relative dissolved gas composition at all (Tab. 2.2).

Because the solubility equilibrium concentrations depend non-linearly on the water temperature (Tab. 2.2), mixing of waters that equilibrated at different temperatures produces apparent supersaturation relative to the temperature of the mixture. Again, the effect is greatest for the heavier gases and minimal for He and Ne. (Ozima and
Podosek, 1983). Resulting supersaturation patterns are consequently not compatible with the excess air signature in groundwater.

Table 2.2: Noble gas composition of air and air-saturated water

<table>
<thead>
<tr>
<th></th>
<th>He</th>
<th>Ne</th>
<th>Ar</th>
<th>Kr</th>
<th>Xe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vol. fract. $z_i$ in dry air [-]</td>
<td>5.24·10^{-6}</td>
<td>1.818·10^{-5}</td>
<td>9.34·10^{-3}</td>
<td>1.14·10^{-6}</td>
<td>8.7·10^{-8}</td>
</tr>
<tr>
<td>$z_i / z_{He}$</td>
<td>1</td>
<td>3.47</td>
<td>1782</td>
<td>0.22</td>
<td>0.017</td>
</tr>
<tr>
<td>$C^* [cm^3 STP/g]$</td>
<td>4.243·10^{-8}</td>
<td>1.754·10^{-7}</td>
<td>2.956·10^{-4}</td>
<td>6.603·10^{-8}</td>
<td>9.019·10^{-9}</td>
</tr>
<tr>
<td>$C^<em><em>i / C</em>{He}^</em>$</td>
<td>1</td>
<td>4.13</td>
<td>6968</td>
<td>1.56</td>
<td>0.21</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Parameter changes relative to $C^*$</th>
<th>$\Delta$He</th>
<th>$\Delta$Ne</th>
<th>$\Delta$Ar</th>
<th>$\Delta$Kr</th>
<th>$\Delta$Xe</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta T = 5.0 , ^\circ C$</td>
<td>-1.55</td>
<td>-3.68</td>
<td>-9.06</td>
<td>-11.4</td>
<td>-13.6</td>
</tr>
<tr>
<td>$\Delta T = 2.0 , ^\circ C$</td>
<td>-0.65</td>
<td>-1.52</td>
<td>-3.81</td>
<td>-4.80</td>
<td>-5.80</td>
</tr>
<tr>
<td>$\Delta T = 1.0 , ^\circ C$</td>
<td>-0.33</td>
<td>-0.77</td>
<td>-1.94</td>
<td>-2.45</td>
<td>-2.96</td>
</tr>
<tr>
<td>$\Delta T = -1.0 , ^\circ C$</td>
<td>0.34</td>
<td>0.79</td>
<td>2.01</td>
<td>2.54</td>
<td>3.10</td>
</tr>
<tr>
<td>$\Delta T = -2.0 , ^\circ C$</td>
<td>0.69</td>
<td>1.61</td>
<td>4.09</td>
<td>5.19</td>
<td>6.34</td>
</tr>
<tr>
<td>$\Delta T = -5.0 , ^\circ C$</td>
<td>1.80</td>
<td>4.19</td>
<td>10.8</td>
<td>13.8</td>
<td>17.0</td>
</tr>
<tr>
<td>$\Delta S = 1 %$</td>
<td>-0.52</td>
<td>-0.56</td>
<td>-0.67</td>
<td>-0.70</td>
<td>-0.72</td>
</tr>
<tr>
<td>$\Delta S = 2 %$</td>
<td>-1.04</td>
<td>-1.12</td>
<td>-1.33</td>
<td>-1.39</td>
<td>-1.43</td>
</tr>
<tr>
<td>$\Delta S = 3 %$</td>
<td>-1.55</td>
<td>-1.68</td>
<td>-1.98</td>
<td>-2.08</td>
<td>-2.14</td>
</tr>
<tr>
<td>$\Delta P = 0.01 , \text{atm}$</td>
<td>1.08</td>
<td>1.08</td>
<td>1.08</td>
<td>1.08</td>
<td>1.08</td>
</tr>
<tr>
<td>$\Delta A = 1·10^{-8} , \text{cm}^3 \text{STP/g}$</td>
<td>1.24</td>
<td>1.04</td>
<td>0.32</td>
<td>0.17</td>
<td>0.10</td>
</tr>
</tbody>
</table>

$z_i$: Volume fraction of gas $i$ in the atmosphere.

$C_i^*$: Concentration of gas $i$ in air-saturated water at solubility equilibrium (20°C, 435 m a. s. l.).

T: Water temperature

S: Salinity

P: Pressure

A: Dissolved excess air volume

$\Delta$ Noble gases: Changes in the noble gas pattern induced by specified changes of the parameters T, S, P and A, relative to the given solubility equilibrium concentration $C^*$. 
Therefore, the additional dissolution of a volume of atmospheric air remains as the only mechanism that is capable of producing a dissolved gas excess with its characteristic atmospheric composition in which the light gases are preferentially enriched.

The question of how this dissolved gas excess can be formed in groundwater is central for the understanding of the excess air phenomenon. Ever since the existence of excess air was first recognized, it has usually been attributed to the dissolution of small air bubbles within the groundwater system. In karstic aquifers, Herzberg and Mazor (1979) explain the supersaturation of atmospheric gases by air suction. During low-discharge periods, air is present in the karstic flow system which can be sucked as excess air in small flow apertures. In the high-discharge season most of the system is water-filled and less air can be sucked in. Hence a negative correlation between water discharge and amount of excess air can be obtained in karstic aquifers.

For sedimentary aquifers, the proposed mechanism of air bubble dissolution remained more vague for many years. To understand, how a gas excess can form from air bubbles in an aquifer, the question of why air bubbles are present in the saturated zone must first be addressed.

### 2.3 Entrapped air

When water moves vertically through the fractal structure of unsaturated natural soils, it usually cannot occupy the complete available pore space. Instead, an air residual will be present in the otherwise water-saturated soil. Similar effects are observable in all type of porous media in which a wetting phase replaces a nonwetting phase. For a soil–groundwater system, the soil air is the nonwetting phase in this process of immiscible displacement. As the capillary forces, that tend to trap the gas phase in a water-wet porous medium dominate over buoyancy and viscous forces, that act to move the gas phase out of the medium, the gas phase is trapped in the water phase.
Entrapped air

Thus, each time vertical water movements are encountered in the transition zone between groundwater and unsaturated zone, small air bubbles are entrapped in the groundwater. The resulting entrapped air is known in soil science for more than sixty years (Christiansen, 1944; McWhorter et al., 1973). The upper aquifer zone, in which periodic water table fluctuations occur and where entrapped air is regularly detectable, is consequently described as the quasi-saturated zone (Faybishenko, 1995). The volume of entrapped air in porous media typically varies between 10 % and 20 % of the total pore space. Depending on the soil type and substrate and on the direction of the water movement, entrapped air volumes range between a few percent and more than 35 %. Table 2.3 summarizes values of entrapped air volumes of different porous media as reported by (Fry et al., 1997).

Entrapped air reduces the hydraulic conductivity of soils and provides an additional natural oxygen source in groundwater. Since the soil air can also comprise contaminants like volatile organic compounds (VOCs), entrapped air may on the other hand also be a long-term source of such contaminants in groundwater.

Obviously, entrapped air is an important element in hydrogeology and subsurface gas exchange. Nevertheless, “the effects that entrapped air has on many practical problems involving remediation have largely been overlooked, and the problem of understanding its role in transient water flow is probably one of the most frequently neglected problems in soil physics” (Faybishenko, 1995).
Table 2.3: Entrapped air values in different soil and substrate types (Fry et al., 1997).

<table>
<thead>
<tr>
<th>Soil / substrate type</th>
<th>Entrapped air</th>
<th>Porosity</th>
<th>Type of experiment</th>
<th>Water flow</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Agricultural soils</td>
<td>4.8–22</td>
<td>n. r.</td>
<td>laboratory</td>
<td>bottom to top</td>
<td>(Smith and Browning, 1942)</td>
</tr>
<tr>
<td>Hesperia sandy loam</td>
<td>15–40</td>
<td>n. r.</td>
<td>laboratory</td>
<td>bottom to top</td>
<td>(Christiansen, 1944)</td>
</tr>
<tr>
<td>Hanford soil</td>
<td>12–21</td>
<td>35–44</td>
<td>laboratory</td>
<td>top to bottom</td>
<td>(Orlob and Radhakrishna, 1958)</td>
</tr>
<tr>
<td>Sintered glass beads</td>
<td>16.4</td>
<td>n. r.</td>
<td>laboratory</td>
<td>bottom to top</td>
<td>(Poulavassilis, 1970)</td>
</tr>
<tr>
<td>Consolidated clays</td>
<td>4.8–6.7</td>
<td>62</td>
<td>laboratory</td>
<td>bottom to top</td>
<td>(Adam et al., 1969)</td>
</tr>
<tr>
<td>Fine sandy loam to loamy sand</td>
<td>4.3–12.6</td>
<td>50</td>
<td>field</td>
<td>top to bottom</td>
<td>(Fayer and Hillel, 1986)</td>
</tr>
<tr>
<td>Los gatos gravelly loam</td>
<td>12</td>
<td>43</td>
<td>field</td>
<td>top to bottom</td>
<td>(Constantz et al., 1988)</td>
</tr>
<tr>
<td>Diablo sandy loam</td>
<td>4</td>
<td>45</td>
<td>field</td>
<td>top to bottom</td>
<td>(Constantz et al., 1988)</td>
</tr>
<tr>
<td>Olympic sand</td>
<td>19</td>
<td>36</td>
<td>field</td>
<td>top to bottom</td>
<td>(Constantz et al., 1988)</td>
</tr>
<tr>
<td>Aiken loam</td>
<td>12</td>
<td>51</td>
<td>field</td>
<td>top to bottom</td>
<td>(Constantz et al., 1988)</td>
</tr>
<tr>
<td>Aiken aggregates</td>
<td>6.9</td>
<td>69</td>
<td>laboratory</td>
<td>bottom to top</td>
<td>(Stonestrom and Rubin, 1989)</td>
</tr>
<tr>
<td>Oakley sand</td>
<td>12.6</td>
<td>37</td>
<td>laboratory</td>
<td>bottom to top</td>
<td>(Stonestrom and Rubin, 1989)</td>
</tr>
<tr>
<td>Loam</td>
<td>8–10</td>
<td>43</td>
<td>laboratory</td>
<td>top to bottom</td>
<td>(Faybishenko, 1995)</td>
</tr>
</tbody>
</table>

**Entrapped air:** Given in percent of the total pore space.

**Porosity:** Given in percent of the total bulk volume.

**n.r.:** not reported.

**Water flow:**
- *bottom to top:* Water saturation from the bottom of the soil column to the top in upward direction.
- *top to bottom:* Water saturation from the top of the soil column to the bottom in downward direction.
2.4 Excess air formation – Part 1

Entrapped air in the uppermost groundwater zone seems to be intrinsically related to the excess air component. It is obvious that entrapped air sets the fundamental basis for the formation of excess air. So far, the conceptual processes involved in the formation of excess air can be summarized as follows (Fig. 2.2).

**Figure 2.2:** Present conceptual picture of the formation of excess air in quasi-saturated porous media. The linking of entrapped air and excess air seems obvious, but a detailed knowledge of how actually entrapped air is dissolved and excess air is formed is still lacking.
Due to vertical water movements in the unsaturated zone, air bubbles are entrapped in the otherwise water-saturated matrix. With increasing hydrostatic pressure, these entrapped air bubbles can be dissolved – either completely or partially. As a result, a dissolved gas excess is present in groundwater. The hydrostatic pressure within the groundwater body usually prevents this dissolved gas excess from degassing, either diffusively or otherwise.

In this rough sketch, a number of important questions still remain unanswered:

1. What are the responsible parameters and/or processes that lead either to a complete bubble extinction or only to a partial bubble dissolution?
2. What are the responsible parameters and/or processes that control the amount of excess air?
3. What are the responsible parameters and/or processes that control the elemental and isotopic composition of the dissolved gas excess?

The existing approach to explain the excess air formation in groundwater is obviously simplified and directed mainly towards obtaining specific “good” results, i.e. most precise temperatures that prevailed during groundwater recharge (see Chapter 3). It focuses on dissolved gas patterns that can be found in natural groundwater systems and neglects any physically sound process-oriented understanding of the excess air formation in quasi-saturated substrates. It is very important to note that obtaining such a more detailed knowledge about the formation of excess air is not only a theoretical challenge. Since excess air is a fundamental property of all groundwaters, it can affect all aspects of the exchange of gases between groundwater and soil air. Among these, important applications like groundwater remediation purposes and possible groundwater contamination can be identified that certainly have to be based on a more thorough understanding of mass transfer between groundwater and soil air. A physically-based explanation of excess air formation in quasi-saturated media would therefore be highly desirable.
Chapter 3

Conceptual excess air models

Looking at measured noble gas concentrations in groundwater samples, by far not all groundwaters do show excess concentrations that have the elemental composition of atmospheric air. To interpret such type of “fractionated” gas supersaturation, simple conceptual approaches that focus on the final state of gas exchange between soil air, entrapped air and groundwater were developed. The physical mechanisms included in these conceptual descriptions of excess air are rather simplistic, and hence the representation of the relevant processes that lead to the formation of excess air is clearly limited in a physical sense. Because these concepts do neither include kinetics nor structural details, such as the spatial and size distribution of entrapped air bubbles, they may be seen as simplified “lumped-parameter” models. Such types of models are not intended to explain mechanistically the excess air formation, their objectives are a simple parameterization of excess air which allows the separation of the measured gas concentration in an equilibrium component and in an atmospheric excess. Because the separation of noble gas concentrations is essential for the noble gas based determination of paleorecharge conditions, all available and presented modeling approaches originated from geochemical or hydrological studies that utilize noble gases in groundwaters.
3.1 Pure excess air model

The concept of excess air generation from the complete dissolution of an additional air volume is shown in Figure 3.1. Therein, the dissolvable air volume is characterized as entrapped air bubbles. If the entrapped air is completely dissolved, we expect an supersaturation pattern that has the composition of pure atmospheric air. This unFractionated excess air (UA) concept is parameterized by the concentration $A_{UA}$ of dissolved dry air in water, the volume fraction $z_i$ of the considered gas in dry air, and the moist air solubility equilibrium concentration $C_i^*$ at the given temperature $T$, atmospheric pressure $P$ and salinity $S$ (e.g.; Heaton and Vogel, 1981).

\[ C_i(T, S, P, A_{UA}) = C_i^*(T, S, P) + A_{UA} \cdot z_i \]

**Figure 3.1:** Unfractionated excess air in groundwater: Formation concept, resulting noble gas supersaturation pattern and model formulation.
3.2 Partial re-equilibration model

In contrast to the simple concept of complete air bubble dissolution, groundwaters sometimes show a different type of excess air composition. In this case, the gas excess exhibits a systematic, mass-dependent fractionation relative to atmospheric air which can be characterized as an increasing enrichment or decreasing depletion with increasing atomic mass. To explain such an supersaturation pattern, Stute et al. (1995) proposed the partial diffusive degassing of an initial excess with atmospheric composition across the groundwater table (Partial re-equilibration model, Fig. 3.2).

\[
C_i(T,S,P) = C_i^*(T,S,P) + A_{PR} \cdot z_i \cdot e^{-\frac{D_i}{D_w}}
\]

**Figure 3.2:** Fractionated excess air in groundwater due to the partial re-equilibration: Formation concept, resulting noble gas supersaturation pattern and model formulation.

As the diffusion coefficients in water are the greater the lighter the gas is, this diffusive re-equilibration affects the light noble gases the most. The partial re-equilibration model that describes the effect of a diffusively controlled gas loss uses as model parameters the amount of initial dissolved excess air $A_{PR}$ and the degree of elemental...
fractionation $F_{PR}$ (Stute et al., 1995; Aeschbach-Hertig et al., 1999). As the duration of the diffusive re-equilibration is the same for all gases, this characteristic time can be implicitly parameterized by the gas loss expressed as the $\Delta$Ne remaining in the water phase. $F_{PR}$ can therefore be interpreted as being proportional to the time during which the initial supersaturation is lost to the soil air. Fractionation of the gas excess in the PR-model occurs solely due to differences in the molecular diffusivities between the gases.

The most obvious physical caveat of the PR model is the need for a relatively large initial dissolved excess $A_{PR}$ to explain typical noble gas patterns in groundwaters. Although $A_{PR}$ may reach values that correspond to $\Delta$Ne values of a few thousand percent, such large initial supersaturation values have never been found in natural systems. In addition they are not compatible with the usual hydrostatic pressures in the zone of groundwater level fluctuations which are far too small to keep such amounts of excess air in solution. Conceptually, this problem can be overcome by assuming a multi step re-equilibration. To explain an observed noble gas pattern, not only one single cycle of air injection and subsequent gas loss is assumed, but a continuous series of cycles of smaller air injections followed by degassing steps, which can yield nearly the same result. In each step a smaller amount of excess air is needed to be injected into the water body and hence the obvious non-realistic assumption of the PR-model vanishes.

In conclusion, this multi step re-equilibration circumvents on the one hand the unrealistically large initial gas excess amounts of the single step approach, on the other hand it represents in a more physically based manner the natural process of cyclic groundwater level fluctuations.
3.3 Closed-system equilibration model

Because in practice many observed noble gas patterns that exhibit an obvious fractionation cannot be explained with the PR model, Aeschbach-Hertig et al. (2000) suggested a new concept for the formation of fractionated excess air. They postulate the equilibration of a finite water volume with a finite air volume under the slightly increased hydrostatic pressure in the quasi-saturated zone (Closed-system equilibration, Fig. 3.3).

\[ c(T,S,P) = \frac{(1-F_{CE}) \cdot A_{CE} \cdot z_i}{F_{CE} \cdot A_{CE} \cdot z_i / c(T,S,P)} \]

Figure 3.3: Fractionated excess air in groundwater due to closed-system equilibration: Formation concept, resulting noble gas supersaturation pattern and model formulation.

The CE concept assumes a closed system in which a finite water volume equilibrates with a finite entrapped air volume under increased pressure. If the air volume is completely dissolved, the result is pure, unfractionated excess air. If not, the elemental compositions of both the dissolved gas and the remaining gas volume are fractionated depending on the initial air–water volume ratio and the pressure on the system. As a
result, the heavy noble gases Ar, Kr and Xe are enriched in the water phase relative to the light noble gases He and Ne.

The CE model also uses two parameters to describe the fractionation process: $A_{CE}$ denotes the initial amount of entrapped air, $F_{CE}$ the reduction of volume of entrapped air due to dissolution resulting from the pressure increase (hydrostatic excess pressure). Fractionation according to the CE model does not depend on the molecular diffusion coefficients but on the differences in the Henry coefficients between the gases and on the change in the ratio of water volume to volume of entrapped air.
Chapter 4

A kinetic model of gas bubble dissolution in groundwater and its implications for the dissolved gas composition

Johannes Holocher, Frank Peeters, Werner Aeschbach-Hertig, Wolfgang Kinzelbach, and Rolf Kipfer

Abstract

Bubble-mediated mass transfer is of major importance for the gas exchange between soil air and the saturated zone. Although the mass transfer between entrapped gas bubbles in the upper, quasi-saturated aquifer zone and groundwater is an essential element in tracer hydrology and in groundwater remediation measures, to our knowledge no model is available that describes the bubble-mediated gas exchange in detail. Hence, a kinetic multi-species model for dissolved gas transport in a porous medium including inter-phase mass transfer with entrapped gas bubbles was developed. This kinetic bubble dissolution (KBD) model takes into account changes in the entrapped gas bubble sizes resulting from the mass exchange and therefore allows the quantification of mass transfer between bubbles of any gas composition and flowing or stagnating water in a substrate column. Resulting from the bubble dissolution, the concentrations of the dissolved atmospheric gases exceed their solubility equilibrium concentrations. The temporal evolution of the composition of this supersaturation is controlled by the actual flow condition and by the physical properties of the aquifer, such as the entrapped air–water ratio in the pore space. Detailed studies of the dissolved gas composition within the system water-gas bubble-matrix can easily be realized using the KBD model.

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4.1 Introduction

The interaction of gas bubbles with a surrounding liquid is an essential part in both natural and technical gas exchange processes. In chemical engineering systems, the dissolution of a discrete gas phase that bubbles through either liquid or liquid-solid reactors is an important application. Factors controlling the flux of gas into the liquid are the rising velocity of the gas bubbles and the bubble size distribution (Leonhard and Houghton, 1963; Lochiel and Calderbank, 1964; Takemura and Yabe, 1998). Considering natural environments, the ocean-atmosphere mass transfer is a prominent example of a bubble-mediated gas exchange process. Small air bubbles introduced by breaking waves are dissolved in the near-surface water column, altering the overall water-air gas exchange (Broecker and Siems, 1984; Memery and Merlivat, 1985). Technically, the concept of bubble-mediated gas transfer has successfully been employed in oxygen bubble plumes to enhance the restoration of deep stratified lakes (Wüest et al., 1992).

In subsurface hydrology, air bubbles entrapped in the quasi-saturated zone can influence the transport dynamics of dissolved gas components in groundwater. Artificially added helium used in tracer experiments is retarded in the presence of entrapped air bubbles which can complicate the correct interpretation of the tracer data (Gupta et al., 1994). Injected oxygen used for in-situ bioremediation of groundwater contaminants can be retarded by entrapped air bubbles as well (Fry et al., 1995). This is of importance since the activity of aerobic micro-organisms and hence the effectiveness of in-situ bioremediation strongly rely on the availability of injected oxygen. However, even under natural conditions air bubbles that are entrapped during cyclic groundwater level rise can serve as oxygen source in groundwater. Especially in aquifers with a dissolved oxygen deficiency, these entrapped air bubbles may be essential for the oxygen supply of aquatic organisms.

Except as the sink or source function for one specific gas component, entrapped air bubbles are usually not included conceptually in any further gas exchange calculation between groundwater and soil air. Correspondingly, the incorporation of entrapped air
bubbles into modeling of dissolved gas transport so far focused only on the retardation effect (Fry et al., 1995; Donaldson et al., 1997) or on the oxygen input to anoxic waters (Williams and Oostrom, 2000).

The requirements for a dissolved gas transport model are completely different if we consider all gases present in the bubbles. Here, changes in the bubble sizes resulting from the mass transfer between water and bubbles, the consequent modification of the relative gas composition in the bubbles and the effect of mass transfer for all dissolved gases have to be included in a transport model. Applications of such a model can be the mass transfer for multi-species liquid or volatile organic contaminants in the upper groundwater zone or the exchange of rare gases used as environmental tracers between entrapped air bubbles and groundwater. Focusing on environmental tracers, the excess air phenomenon is an important example of a bubble-mediated gas exchange between groundwater and soil air. If conservative atmospheric trace gases such as the noble gases (He, Ne, Ar, Kr, Xe) or sulfur hexafluoride SF₆ are used as environmental tracers in groundwater, an omnipresent supersaturation of these gases is evident. As the elemental composition of the dissolved gas excess is similar to that of atmospheric air, it is called “excess air” (Heaton and Vogel, 1981).

Excess air is a ubiquitous attribute of all groundwaters and since its first recognition, its formation has been attributed to the dissolution of entrapped air bubbles in the uppermost groundwater zone. Unfortunately, the excess air component can strongly influence the interpretation of gaseous tracers in groundwater. Noble gas based paleoclimate reconstruction (Stute et al., 1995; Beyerle et al., 1999; Aeschbach-Hertig et al., 2000) and groundwater dating with the ³H-³He method (Schlosser et al., 1988; Holocher et al., 2001) or with SF₆ (Busenberg and Plummer, 2000) can be affected. Therefore it is essential to understand the processes involved in the formation of excess air in detail. To this end, we present a kinetic model for dissolved gas transport in a porous medium including inter-phase mass transfer with entrapped air bubbles. It includes all major atmospheric gases as well as changes in the entrapped air bubble sizes resulting from the mass exchange and therefore allows detailed studies of the dissolved gas composition within the system water-bubble-matrix.
4.2 Theory

We consider entrapped air bubbles in the upper, quasi-saturated groundwater zone. A control volume of a water-filled porous medium is assumed to contain entrapped air bubbles. Such entrapped air bubbles resulting from naturally occurring vertical water movement are spatially fixed since the capillary forces that act to trap the gas phase usually dominate over the buoyancy forces in a natural porous medium (Fry et al., 1997). The bubbles are assumed to be homogeneously distributed in the considered control volume. The maximum size of an entrapped air bubble is limited by the individual pore diameter. The soil matrix is always covered by a water film that increases in thickness with increasing water content (Kutilek and Nielsen, 1994). It can therefore reasonably be assumed that the air bubbles are completely surrounded by water. The total pore space $V_{pore}$ of the control volume is given by:

$$V_{pore} = V_{tot} \cdot \theta = V_a + V_w = V_w (1 + r_{a-w})$$

(4.1)

$V_{tot}$ is the control volume, $\theta$ is the total porosity, $V_a$ is the air-filled and $V_w$ the water-filled pore volume. $V_a$ and $V_w$ are related via the air-water ratio $r_{a-w} = V_a/V_w$. For the derivation of the governing equations, we assume that all entrapped air bubbles have the same size. Hence the number of bubbles in the control volume is given by

$$n_{Bubbles} = V_a \cdot \left(\frac{4}{3} \pi r_{Bubble}^3\right)^{-1}.$$ 

If an air bubble is introduced into a water body that initially was in solubility equilibrium with the atmosphere, gas will be transferred from the bubble into the water as a result of the pressure that acts on the bubble. This pressure is the sum of the hydrostatic pressure given by the depth of the bubble in the water body and the capillary pressure resulting from the surface tension of the curved bubble surface. The inter-phase mass flux is proportional to the concentration deficit in the water phase and can be described for gas $i$ by:

$$J_i = k_i (C_{w,i} - C^*)$$

(4.2)
Theory

where $J_i$ is the mass flux of the considered gas $i$ from the aqueous phase to the gas phase, $k_i$ is the mass transfer coefficient [m·s⁻¹], $C_{w,i}$ is the actual aqueous phase concentration [mol·m⁻³] and $C^*_i$ is the equilibrium concentration in the aqueous phase [mol·m⁻³]. Expressing the equilibrium concentration in water by Henry's law, the mass transfer is written as:

$$J_i = k_i \left( C_{w,i} - \frac{p_i}{RTK_{H,i}} \right)$$  \hspace{1cm} (4.3)$$

$K_{H,i}$ is the dimensionless Henry coefficient for the considered gas, $p_i$ is the partial pressure of the gas in the air bubble [Pa], $R$ is the universal gas constant [Pa·m³·K⁻¹·mol⁻¹] and $T$ is the water temperature [K].

The determination of the correct $k_i$ value for bubble-mediated gas transfer can be crucial. Depending on the considered system, several different formulations for $k$ can be found in the literature. An overview of the underlying concepts is given in (Clift et al., 1978) and (Cussler, 1997). Leonhard and Houghton (1963) and Takemura and Yabe (1998) summarize $k$ values for rising bubbles in liquid reactors. Conceptually, the mass transfer between an immobile small entrapped gas bubble and groundwater for volatile gases is limited by a diffusively-controlled stagnant water film around the bubble. Within the bubble, mixing processes in the gas phase are fast and hence the gas phase can be described as homogeneous. In our model we assume the mass transfer coefficient to depend on the water flow condition. Two situations are distinguished: Bubbles in a stagnant fluid (no-flow regime) and air bubbles that are passed by flowing water (advective regime).

In case of no flow, the mass transfer coefficient $k$ for a spherical structure is given by Schwarzenbach et al. (2002):

$$k_i = \frac{D_{\infty,i}}{\delta_{eff}} = D_{\infty,i} \left( \frac{1}{r} + \frac{1}{\delta} \right)$$  \hspace{1cm} (4.4)$$
$D_{w,i}$ is the gas specific diffusion coefficient in water [m$^2$·s$^{-1}$]. $\delta$ is the thickness of the stagnant, diffusively controlled film layer in the liquid around the sphere [m]. In no-flow conditions and for small bubble radii, the term $r^{-1}$ dominates over $\delta^{-1}$. The effective boundary layer thickness $\delta_{\text{eff}}$ is therefore proportional to $r$, and consequently $k_i = D_{w,i} \cdot r^{-1}$.

For advective flow regimes, the boundary layer thickness depends on the flow velocity $v$. In this case we use from Epstein and Plesset (1950):

$$k_i = D_{w,i} \left( \frac{1}{r} + \frac{1}{\sqrt{\pi D_{w,i} \tau}} \right) = D_{w,i} \left( \frac{1}{r} + \sqrt{\frac{v}{2\pi r D_{w,i}}} \right)$$

(4.5)

$\tau$ is the contact time, i.e. the time a water parcel with flow velocity $v$ needs to pass by a bubble with diameter $2r$.

The rate of change of dissolved mass for gas $i$ in each spherical air bubble can be expressed by:

$$\frac{dn_i}{dt} = -A_{\text{int}} \cdot J_i = -A_{\text{int}} k_i (C_{w,i} - C_i^*) = -A_{\text{int}} k_i \left( C_{w,i} - \frac{p_i}{RTK_{H,i}} \right)$$

(4.6)

$$= -4\pi r^2 k_i \left( C_{w,i} \frac{x_i}{S_i} \left( p_{\text{am}} - p_w + \rho gh + \frac{2\sigma}{r} \right) \right)$$

$n_i$ is the exchanged amount of gas [mol], $A_{\text{int}}$ the interfacial area [m$^2$], $r$ is the bubble radius [m], $p_i$ is the actual pressure of gas $i$ within the bubble [Pa], $x_i$ is the mol fraction of gas $i$ in the atmosphere [-], $p_{\text{am}}$ is the barometric pressure [Pa], $p_w$ is the partial pressure of the water vapor in the bubble [Pa], $\rho \cdot g \cdot h$ is the hydrostatic pressure at depth $h$ [Pa], $2\sigma r^{-1}$ is the capillary pressure according to the curvature of the bubble surface [Pa] with the surface tension $\sigma$ [Pa·m] and $S_i = RTK_{H,i}$ is the solubility of gas $i$ [Pa·m$^3$·mol$^{-1}$].
To describe the dissolution of an entrapped air bubble and its effect on the dissolved noble gas concentrations, we assume the bubble to consist of the noble gases He, Ne, Ar, Kr and Xe and the main air constituents nitrogen and oxygen. The total gas exchange per unit time is then given by the sum of the changes of all considered gases:

\[
\frac{dn_{\text{tot}}}{dt} = \sum_i \frac{dn_i}{dt} = -4\pi r^3 \sum_i k_i \left( C_{w,i} - \frac{S_i}{S} \left( p_{am} - p_w + \rho gh + \frac{2\sigma}{r} \right) \right)
\]

with \( i = \text{He, Ne, Ar, Kr, Xe, N}_2, \text{O}_2 \).

The associated change in bubble radius with time is described by:

\[
\frac{dr}{dt} = \frac{3RT}{4\pi r} \left( \frac{1}{4\sigma + 3r \left( p_{am} - p_w + \rho gh \right)} \right) \frac{dn_{\text{tot}}}{dt}
\]

Referring to concentrations in water, the temporal evolution of dissolved gas \( i \) considering different bubble radii classes is:

\[
\frac{dC_{w,i}}{dt} = \sum_r \frac{n_{\text{bubble},r} A_{\text{surf},r} J_{i,r}}{V_w} = \sum_r \frac{n_{\text{bubble},r}}{V_{\text{tot,0}}} \left( \frac{V_{\text{tot,0}} \theta}{1 + r_{g,w}} \right) \frac{dn_{i,r}}{dt}
\]

with \( C_{w,i} \) the dissolved concentration of gas \( i \) [mol·m\(^{-3}\)], \( n_{\text{bubble},r} \) the number of bubbles in the respective size class, \( A_{\text{surf},r} \) the surface area of a bubble in that class [m\(^2\)] and \( J_{i,r} \) the mass flux of gas \( i \) in the considered bubble radius class.

The coupled differential equations (4.7) to (4.9) are the governing model equations for the mass transfer between water and entrapped air bubbles.

To obtain the differential equations describing aqueous phase transport of the dissolved gases, we combine the mass conservation statement for a control volume with the well-known advection-dispersion equation (Bear, 1972). The one-dimensional vertical flow is given by:
The KBD-model

\[ \frac{\partial (\theta_w C_{w,i})}{\partial t} = \frac{\partial}{\partial z} \left( \theta_w D_z \frac{\partial C_{w,i}}{\partial z} - \theta_w v C_{w,i} \right) + B = \frac{\partial}{\partial z} \left( \theta_w D_z \frac{\partial C_{w,i}}{\partial z} - q C_{w,i} \right) + B \quad (4.10) \]

\( \theta_w \) is the water-filled porosity [-], \( C_{w,i} \) is the dissolved concentration [mol·m\(^{-3}\)], \( D_z \) is the hydrodynamic dispersion coefficient in flow direction [m\(^2\)·s\(^{-1}\)], \( v \) is the aqueous phase velocity [m·s\(^{-1}\)] and \( q \) is the water flux [m·s\(^{-1}\)]. \( B \) represents the source term that results from the mass transfer between water and entrapped air bubbles given in equation (4.9). Note that \( \theta_w \) is assumed to increase with dissolution of the gas bubbles.

Finally, equations (4.7) to (4.10) completely describe the dissolved gas transport in the presence of entrapped air bubbles in groundwater. These model equations are solved numerically employing a fully implicit finite difference code. The underlying modeling procedure is summarized in Figure 4.1.

The large surface area-to-volume ratio of the entrapped gas bubbles facilitates the inter-phase gas exchange. Furthermore, the distribution of the entrapped gas bubbles in the water phase is assumed to be homogeneous in the horizontal which implies that the spatial interval between the bubbles is always small. For example, if we assume \( \theta = 0.4, r_{a-w} = 0.1 \) and \( r_{\text{bubble}} = 0.3 \) mm, the average distance between two adjacent bubbles is \( 4.3 \times 10^{-5} \) m. Even with a strictly diffusive mass transfer in water, for a gas like Xe the characteristic travel time between such bubbles is in the order of 1 s. As a result, the numerical representation of the model considers each modeled depth to be homogeneous with regard to the concentrations of the dissolved gases.

For the aqueous phase, a prescribed constant water outflow \( q_{\text{out}} \) is used at the bottom of the modeled aquifer column. To ensure that \( q_{\text{out}} \) is constant over the whole simulation period, changes in the water-filled porosity at each depth caused by air bubble dissolution are compensated by respective changes in the water flow \( q \). Thus, at the top of the column \( q \) is given by:
This implies that $q(z=0)$ is adjusted instantaneously to balance the variable water-filled porosity and to ensure a constant water outflow $q_{out}$.

The initial composition of the gas phase is pre-set to atmospheric values. The initial dissolved concentrations are usually at solubility equilibrium for the given temperature, salinity and barometric pressure, but they may as well be changed to model other specific situations. From the given bubble sizes, initial bubble radii profiles for different depths are calculated assuming pressure equilibrium between the surrounding water and the bubbles at depth $h$ by solving the cubic equation:

$$r^3(h) = \frac{3NRT}{4\pi(p_{am} - p_w + \rho gh + 2\sigma \cdot r(h)^{-1})} \quad (4.12)$$

$N=(n_{He}+n_{Ne}+n_{Ar}+n_{Kr}+n_{Xe}+n_{N2}+n_{O2})$ is the total initial amount of gas in a bubble of the specified size at atmospheric pressure.

In the final phase of the bubble dissolution when the bubble volume tends to zero and the capillary pressure evolves to infinity, the following rigorous scheme is utilized in the numerical simulation: If the number of moles of any conservative gas in the bubble reaches zero, the bubble is immediately forced to dissolve completely. This means that the remaining amounts of all other gases are transferred into the water, and the bubble radius at the end of the time step is set to zero. This procedure is based on the observation that in a liquid, smallest gas bubbles collapse under the influence of the enlarged capillary pressure and that the final bubble dissolution phase is irreversible. Numerically, variable time steps are used in the model. To resolve the final dissolution stage correctly, before the bubble extinction the time step size is consecutively reduced to 1s.
Chapter 4: The KBD-model

Figure 4.1: Simplified flow chart of the KBD model.
4.3 Results and discussion

The kinetic bubble dissolution (KBD) model describes an efficient method to assess the relevance of entrapped gas bubbles on the solute transport in porous media. While virtually any kind of entrapped gas can be considered in the model – provided its solubility and its molecular diffusivity in water is known – we will focus on entrapped air bubbles with atmospheric composition being present in the upper, quasi-saturated groundwater zone. To elucidate the capabilities of the model, we discuss in the following results of a set of simulations employing various model parameters.

4.3.1 Illustrative model application

For a more detailed insight into the physical concepts of the KBD model, results of a model simulation of a 1 m sand column are presented in Figure 4.2. The model parameters used in this simulation are given in Table 4.1. In the simulation, a vertical spatial discretization of 1 cm was employed. Two different scenarios were considered: an advective flow regime with vertical water flow in the simulated substrate column, and a stagnating situation without advective transport. Except for the flow velocity and the dispersion coefficient associated with the flow, the model parameters are identical in the two scenarios.

**Stagnant flow regime**

For the stagnant conditions, the entrapped air bubbles in the simulated 1 m aquifer column dissolve only partially (Fig. 4.2a). As a result of the increased pressure acting on the bubbles, gas will be transferred into the water until a new equilibrium condition between the surrounding water and the remaining gas phase is reached.
Table 4.1: Model parameters used in the KBD model simulations

<table>
<thead>
<tr>
<th>Model Parameter</th>
<th>Standard</th>
<th>4 Bubble Classes</th>
<th>Hydrostatic Overload</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column length</td>
<td>1 m</td>
<td>1 m</td>
<td>1 m</td>
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<tr>
<td>Number of bubble classes</td>
<td>1</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>Initial bubble radius in class</td>
<td>0.35 mm</td>
<td>0.25 – 0.3 – 0.35 mm</td>
<td>0.35 mm 0.35 mm 0.4 mm</td>
</tr>
<tr>
<td>Total porosity</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>Air-water ratio</td>
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<td>0.1</td>
<td>0.2</td>
</tr>
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<td>Water temperature</td>
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<td>Atmospheric pressure</td>
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<td>1 atm</td>
<td>0.9615 atm</td>
</tr>
<tr>
<td>Hydrostatic overload</td>
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<td>0 atm</td>
<td>0.02 atm</td>
</tr>
<tr>
<td>Salinity</td>
<td>0 %</td>
<td>0 %</td>
<td>0 %</td>
</tr>
<tr>
<td>Specific vertical water flux</td>
<td>10 cm/h</td>
<td>10 cm/h</td>
<td>10 cm/h</td>
</tr>
<tr>
<td>Water flux stagnant regime</td>
<td>0 cm/h</td>
<td>0 cm/h</td>
<td>–</td>
</tr>
<tr>
<td>Initial water concentration</td>
<td>$C_{equi}$</td>
<td>$C_{equi}$</td>
<td>$C_{equi} + 8 \cdot 10^{-4} \text{cm}^3 \text{ air} / \text{gr water}$</td>
</tr>
</tbody>
</table>

The relative change in bubble size is the greater, the larger the hydrostatic pressure and hence the depth is. Analogously, the time to reach equilibrium between the entrapped gas phase and the surrounding water increases with depth.

Figure 4.2b shows relative concentrations of the noble gases He, Ne, Ar, Kr and Xe and of oxygen and nitrogen at the bottom of the modeled column for stagnant conditions. The diffusivities of the gases in water and their solubilities are given in Table 2.1.

Starting from solubility equilibrium ($C / C_{ini} = 1$) at the given temperature, salinity and pressure, the dissolved concentrations are rising for all gases as a result of the mass transfer from the gas bubbles into the water.
Results and discussion

Figure 4.2: Bubble radii and relative outflow concentrations of He, Ne, Ar, Kr, Xe, N₂ and O₂ from the KBD model simulation using the model parameters shown in Table 4.1. Fig. 4.2a and 4.2b show the results for stagnant, no-flow conditions. Fig. 4.2c and 4.2d display the simulations for an advective vertical downward water flow in the modeled aquifer column.

The final degree of concentration increase is entirely controlled by the solubility of the gases: The better soluble the gas, the smaller the relative rise. Therefore the response of gases with a low solubility such as He and Ne is most sensitive to air injection and can indicate the presence of dissolved excess air. The resulting new dissolved gas composition equals the prediction of the excess air model describing bulk dissolved gas abun-
dance patterns in groundwater as the result of closed-system equilibration between entrapped air and a stagnant water body (Aeschbach-Hertig et al., 2000). The transition from the initial condition towards the new equilibrium is influenced by the diffusivities of the gases in water. The time to reach the new equilibrium concentrations decreases with increasing diffusivities of the gases. This is illustrated in the concentration profiles of argon, nitrogen and oxygen. The concentrations of nitrogen and oxygen that diffuse more slowly in water than Ar are also rising slower than the Ar concentrations. But as Ar is better soluble, the final degree of supersaturation is larger for oxygen and nitrogen than for Ar. As a result, the oxygen and nitrogen concentration curves cross the Ar concentration curve before reaching the final equilibrium state (Fig. 4.2b).

Generally, the temporal scale of the equilibration between entrapped air and closed water phase depends on the initial bubble size distribution and on the air-water ratio in the pore space. An increasing amount of entrapped gas in relation to the water volume leads to a prolongation of the equilibration time. If the air-water ratio is considered constant, a distribution of the entrapped air volume in small bubbles facilitates the equilibration process and hence results in a shorter equilibration time compared to that based on larger bubbles.

**Advective flow regime**

If we assume a vertical downward water flow in the modeled substrate column, the entrapped air bubbles dissolve completely (Fig. 4.2c). Due to the permanent supply of water that is undersaturated with respect to the local pressure at a considered depth, a continuous mass transfer from the entrapped gas bubbles into the water takes place. As a result, the entrapped air is finally completely dissolved. The time needed for the complete air bubble extinction is orders of magnitudes larger than the time that is required for establishing new equilibrium conditions in the stagnant regime. In Figure 4.2c, the bubble radii in the uppermost and in the lowermost three depth levels is shown with time. Regarding the chronology of the bubble collapses at the different depths, two competing mechanisms that influence the evolution of the bubble ex-
tinction within the vertical column are evident. The hydrostatic pressure acting on the bubbles favors a bubble dissolution sequence from bottom to top (Depth 0.995–0.975 m, Fig. 4.2c) whereas the fresh water flushing of the column enhances the extinction from the top to the bottom of the column (Depth 0.005–0.025 m, Fig. 4.2c). Depending on the flow velocity, the air-water ratio in the pore space, the column length and the initial bubble sizes, any kind of spatial sequence of bubble dissolution is possible.

In Figure 4.2d, the relative dissolved gas concentrations in the outflow are shown for the vertical water flow regime. Compared to the time scale for the complete dissolution process, the first adaptation of the dissolved concentrations in response of the application of pressure on the entrapped air occurs very fast. Therefore the concentrations rise rapidly from solubility equilibrium to the initial solubility-controlled supersaturation pattern that resembles the final state of the stagnant simulation. Afterwards, the relative concentrations of the different gases evolve in different ways. The concentrations of the gases of low solubility increase whereas those of the heavier gases with a high solubility decrease. This is explained by the solubility-controlled changes in the relative gas composition of the entrapped gas phase (Fig. 4.3). The total gas pressure in the bubbles is dominated by nitrogen that has the highest abundance of all considered gases. As a result, the relative contribution of nitrogen to the gas composition remains nearly constant throughout the whole bubble dissolution process. In contrast and as direct result of the enhanced mass transfer into the water, the mole fractions of the well soluble gases such as Kr or Xe decrease in the gas phase, which in turn causes a relative decrease in the dissolved concentration of these gases. Due to the low solubility of the light noble gases, their mole fraction is enlarged during the bubble dissolution process, resulting in the equivalent increase in the dissolved concentrations as shown in Figure 4.2d. After these concentration changes, a plateau-like phase with a nearly constant concentration pattern is reached that resembles a quasi-steady state condition, although the dissolution process is still continuing. This quasi-steady state is again reached the faster, the better soluble the gas is.
Figure 4.3: Relative gas composition of the dissolving gas phase for the vertical advective water flow regime in the lowermost depth class.

After the entrapped gas volume is completely removed, the concentrations in the column outflow decrease towards the prescribed solubility equilibrium concentrations for all gases.

With the extinction of the entrapped air bubbles in the lowermost column box, a small peak is manifest in the dissolved concentrations of all gases (Fig. 4.2d). This increase reveals the transfer of the remaining gas volume into the water volume at the depth associated with the bubble collapse. Because the light gases with a low solubility react most sensitively to air transfer, they show the most pronounced peak, whereas for the heavy noble gases the reaction to this air transfer is relatively small. The bubble dissolution in the adjacent upstream column boxes also influences the outflow concentrations and generates the second and the third peak, respectively.
4.3.2 Sensitivity of the model to parameters

The influence of the model parameters on the entrapped gas dissolution process was investigated in multiple simulations using a vertical discretization of 10 cm. Figure 4.4 shows the effects of changes in the flow velocity \( v \), in the ratio of entrapped air to water volume \( r_{a,w} \) and in the total porosity \( \Theta \) on the bubble dissolution dynamics and on the calculated dissolved oxygen concentrations in the column outflow. At first sight, the resulting evolution of the bubble radius and of the dissolved oxygen concentration is similar in all cases, no matter what model parameter is looked at. A decrease in the flow velocity \( v \), an increase in the air-water ratio \( r_{a,w} \) as well as an increase in the total porosity \( \Theta \) prolong the dissolution process and raises the oxygen concentration peaks. The vital quantity that controls the dissolution process of entrapped air is the amount of gas – relative to the total entrapped air volume – that can be dissolved per time step in a given water volume. A decrease of \( v \) or an increase in \( r_{a,w} \) therefore prolongs the time needed for a complete bubble dissolution as the amount of entrapped air soluble per time step is reduced. In addition, the final collapse of the entrapped bubbles produces a relatively sharply marked response in the concentrations. In the case of smaller flow velocities, the peak concentrations are less affected by the smoothing effect of dispersion and are only slowly transferred out of the respective column box. In the case of larger air-water ratios, the amount of gas in the final collapse that is transferred into the water is relatively large which causes a stronger effect on the dissolved concentrations. On the other hand, if the flow velocity \( v \) is increasing, the rapid flushing of the column leads to a faster dissolution of the entrapped gas phase and a smoother concentration time series that doesn’t show the influence of the final gas bubble collapse. Similarly, a decrease in the ratio of entrapped air to water leads to a distribution of the dissolved gas on a much larger water volume, hence a more effective gas dissolution process and finally to a much faster bubble extinction with smoother concentration profiles.
Figure 4.4: Influence of the model parameters flow velocity \( v \), air-water ratio \( r_{aw} \) and total porosity \( \theta \) on the bubble dissolution process and the dissolved oxygen concentrations.

Since the water flux \( q \) defined as the product of the total porosity \( \theta \) and the flow velocity \( v \) is considered constant in our model, an increase in the porosity at constant pore size spectrum has the same effect on the entrapped gas dissolution process as a decrease in the flow velocity (Figure 4.4e and 4.4f).

To examine the influence of a distribution of different bubble sizes on the dissolved concentrations, the illustrative model simulations were repeated employing now four different bubble size classes instead of only one single bubble size. The other model parameters were not changed. The results are shown in Figure 4.5. From the bubble radii, we see that a redistribution of the bubble sizes occurs in both scenarios – the vertical flow and the stagnating situation. In both cases, a progression in the bubble extinction sequence exists which begins with the smallest bubbles and ends with the largest bubbles. While the smaller bubbles dissolve, the larger bubbles grow until finally
the last remaining bubble size class is either dissolved completely (advective flow regime) or maintained stable at the new equilibrium with the surrounding water (stagnant flow regime).

**Figure 4.5:** Bubble radii and relative outflow concentrations of He, Ne, Ar, Kr, Xe, N₂ and O₂ from the KBD model simulation for four distinct bubble size classes. Fig. 4.5a and 4.5b show the results for stagnant, no-flow conditions. Fig. 4.5c and 4.5d display the simulations for an advective vertical downward water flow.
The reason for this characteristic behavior is the difference in the local dissolved equilibrium concentrations for different size bubbles. Due to the higher capillary pressure in small bubbles, their local equilibrium concentrations in water are higher than for larger bubbles. Thus in a multi bubble size system the water concentrations that increase with time represent a saturation deficiency only with respect to the smallest bubbles. Considering the larger bubbles these concentrations correspond to a local supersaturation and force the bubbles to grow. As a result, the bubbles will be rearranged in size, leaving only one final bubble class. For this specific bubble size the hydrostatic pressure plus the capillary pressure are balanced by the gas pressure inside the bubble. It can therefore be considered stable.

If the relative concentrations of the multiple bubble size simulations displayed in Figures 4.5c and 4.5d are compared to the results obtained by employing just one single bubble size, it is obvious that the general dynamics of the gas dissolution is nearly identical (Fig. 4.2b and 4.2d). The main differences are small concentration peaks evident in the multi bubble size simulations that result from the extinction of the respective smaller bubble sizes. While the concentration evolution is similar in both cases, the time scale is prolonged in the multi-bubble size simulations, depending on the actual flow regime. Apparently, the re-distribution of the entrapped gas between different bubble sizes becomes the time controlling process considering no flow conditions. In this case, the bubble size rearrangement takes place only diffusively, and hence the time scale is prolonged by a factor of approximately 1400. In the advective flow system, the time until all bubbles are dissolved is only slightly increased. Here, the advective transport of the dissolved gases continues to control the bubble dissolution process.
4.3.3 Comparison of model results and measured data

The applicability of the KBD model was tested by comparing measured noble gas concentrations of a laboratory experiment with simulated data. We present results from a large-scale column experiment using a sand filter in the waterworks of the city of Zürich, Switzerland.

The 1 m × 1120 m² filter of initially dry quartz sand was water-saturated from the bottom of the sand to the top. During this process, air bubbles are entrapped in the sand. In the next step, the water level in the system was raised 20 cm above the sand surface, and a vertical downward water flow through the sand filter was initiated. Due to the constant water supply to and discharge from the sand filter, the hydraulic conditions in the system can be considered constant. The water in the inflow is not in solubility equilibrium with the atmosphere, but it contains already an approximately constant dissolved gas excess with atmospheric composition. This initial supersaturation is the result of the pretreatment of the water in the waterworks. In the operation mode, the air that is entrapped in the first imbibition process is continuously dissolved, resulting in a dissolved gas excess that exceeds the input concentrations and that is detectable at the outflow of the filter very soon after the start.

The parameters of the model simulation are given in Table 4.1 (Hydrostatic overload). Except for the number of bubble classes, the initial bubble radii and the air-water ratio, all parameters are known from the experiment. The three free parameters were optimized to fit the first six measured data points. The measured and the simulated He and Ne data are shown in Figure 4.6.

The model results and the measured data agree very well. The KBD model correctly predicts the initial concentration rise, the following plateau-like phase and the final collapse of the entrapped air bubbles. The small-scale variation in the modeled He concentrations resulting from defined bubble collapses is not expected to be visible in the measured data because of the heterogeneity in the sand filter. Nevertheless, the very good agreement between the overall concentration profile predicted by the KBD model
and the measured data supports the validity of the model and the conceptualizations made within the model.

Figure 4.6: Comparison between measured experimental He and Ne data and simulation results. The experiment investigated the formation of excess air in a quartz sand filter in the waterworks of the city of Zurich, Switzerland. The simulation parameters are given in Table 4.1 (Hydrostatic overload).

4.3.4 Relevance of subsurface bubble-mediated oxygen transfer

Entrapped air bubbles in the upper, quasi-saturated groundwater zone are a relevant source of dissolved gases in groundwater. The dissolution of entrapped air serves in particular as an important oxygen supply for the aquatic fauna in the transition zone between groundwater and soil air. As per volume twenty-eight times more oxygen is contained in entrapped air than is dissolved in water at atmospheric solubility equilibrium at 15 °C (Fry et al., 1997), entrapped air will significantly enhance all biogeochemical processes within the quasi-saturated zone for which oxygen is the rate-limiting factor. Especially in aquifers with cyclic groundwater level fluctuations that stead-
ily refill the entrapped air volume, the bubble-mediated oxygen supply will work most efficiently. Considering anoxic groundwaters, the importance of the bubble-mediated oxygen supply is even larger. Examples for the occurrence of anoxic groundwaters are the downstream zone of In-Situ Redox Manipulations (Williams and Oostrom, 2000) of contaminated aquifers and aquifer systems that are charged by carbon-rich waste water inflows (Ronen et al., 1987).

To demonstrate the importance of entrapped air for the oxygen supply in anoxic environments, we simulated a 1 m aquifer column which is flown through by oxygen-free water (see model parameters in Tab. 4.1). As a result of the entrapped air bubble dissolution, the dissolved oxygen concentrations are rise nearly immediately to a noticeable level (Fig. 4.7a). Due to the bubble extinction from top to bottom of the column, the oxygen concentration in the outflow shows significant oxygen values for a relatively long time. The temporary oxygen input from the upper parts of the column retards the completion of the bubble extinction in the lower column parts (Fig. 4.7 b). The overall oxygen input from the entrapped air bubbles for this simulation is about 4750 cm$^3$ or 3.4 g dissolved oxygen in 24 hrs. To attain this amount of dissolved oxygen solely by diffusion across the groundwater table would take several months. This clearly proves the ecological importance of the bubble-mediated gas exchange in the upper, quasi-saturated aquifer zone.
Figure 4.7: Bubble radii and oxygen concentrations from the KBD model simulation considering anoxic water flowing through the simulated aquifer column.

The example emphasizes the importance of entrapped air bubble dissolution for the dissolved gas budget in groundwater. The presented KBD-model helps in quantifying this type of bubble-mediated gas transfer in porous-media and promises new interesting applications in the field of environmental sciences.
Chapter 5

Experimental investigations on the formation of excess air in quasi-saturated porous media

Johannes Holocher, Frank Peeters, Werner Aeschbach-Hertig, Markus Hofer, Matthias Brennwald, Wolfgang Kinzelbach, and Rolf Kipfer

Abstract

The formation of an excess of dissolved gas ("excess air") in quasi-saturated media was studied by analyzing and interpreting dissolved noble gas concentrations in laboratory column experiments. Using quartz sand filled columns of 1 m length, two different experimental designs were realized. In the first, groundwater recharge was simulated by a unidirectional vertical water flow through the columns. In the second, groundwater level fluctuations in an aquifer zone without active infiltration were reproduced by cyclic water level fluctuations in the columns. The reproducible generation of excess air under these defined, near natural conditions was successful. Partial or complete dissolution of air bubbles entrapped in the quartz sand could be identified as the mechanism responsible for the generation of excess air. Depending on the experimental design, supersaturation of the dissolved atmospheric noble gases ranging between 1.4 % ΔNe and 16.2 % ΔNe was found. The measured noble gas patterns were interpreted using inverse modeling and conceptual gas exchange models and were compared to results of numerical simulations of gas bubble dissolution in water filled soil columns. The gas composition in most of the samples resembles either unfractinated pure atmospheric excess air or is fractionated in accordance with closed-system equilibration between entrapped air and surrounding water. In addition to the amount of entrapped air, the hydrostatic pressure exerted on the entrapped air bubbles is the dominating parameter responsible for the total amount of dissolved air. The composition of the excess air component is controlled by the water flow regime, the bubble size distribution, the initially dissolved gas concentrations and the initially entrapped gas composition.

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5.1 Introduction

Supersaturation of atmospheric gases in groundwater is ubiquitous and manifest in the concentrations of the inert atmospheric noble gases. Since the composition of the dissolved gas excess is often similar to that of atmospheric air, Heaton and Vogel (1981) introduced the term “excess air” for this phenomenon. Excess air was first described by Mazor (1972) for thermal waters of the Jordan Rift Valley, and by Oana (1957), Andrews and Lee (1979) and Heaton and Vogel (1979) in sedimentary aquifers. Whenever trace gases with a low solubility in groundwater are considered, excess air plays an important role. In these cases, usually the equilibrium concentration of the considered gas has to be determined, which implies that the excess air component has to be separated from the total measured dissolved gas concentration. Examples of trace gas methods in groundwater which are sensitive to excess air are the dating of groundwater with $^3$H-$^3$He (Schlosser et al., 1988; Stute et al., 1997; Aeschbach-Hertig et al., 1998) and SF$_6$ (Busenberg and Plummer, 2000), and the determination of paleorecharge conditions, especially the infiltration temperature (Mazor, 1972; Andrews and Lee, 1979; Stute and Schlosser, 1993; Stute et al., 1995). Besides the relevance of excess air for trace gas methods in groundwater, the excess air component itself most probably conveys information about past climatic and recharge conditions as well as aquifer characteristics (Heaton et al., 1986; Wilson and McNeill, 1997; Stute and Talma, 1998; Aeschbach-Hertig et al., 2001). Finally, excess air in groundwater is also important for the biogeochemistry of the transition zone between groundwater and unsaturated zone. As excess air comprises all air components, i.e. also the main air constituents oxygen and nitrogen, a dissolved oxygen source in the uppermost aquifer zone exists which is usually not considered, although it may significantly contribute to the oxygen availability in a groundwater body. Note that the biogeochemical reactivity of oxygen in most cases prevents the direct detection of the excess air component in the dissolved oxygen concentrations in aquifer systems.
Since its first recognition in porous aquifers, the formation of excess air has usually been explained by the complete dissolution of entrapped air bubbles under the influence of the hydrostatic pressure (Heaton and Vogel, 1981). The air entrapment in porous media during water saturation is a well-known effect (e.g., Christiansen, 1944; Faybishenko, 1995). As air entrapment occurs regularly in groundwater systems due to cyclic or periodic water level fluctuations, the dissolution of parts of this additional reservoir of atmospheric gases is most likely and as a result may lead to the excess air component in groundwater.

This concept of linking the dissolution of entrapped air to the formation of excess air has never been directly proven. A detailed knowledge of the processes involved in excess air generation and the identification of the relevant parameters controlling these processes is still lacking. Apart from some work in the 1980s (Tegen, 1988; Gröning, 1989; Osenbrück, 1991), conclusive investigations on the generation of excess air under defined laboratory conditions have never been conducted. In this study we therefore performed laboratory column experiments to (1) reproducibly generate excess air, (2) identify the relevant mechanism that leads to excess air and (3) identify the underlying physical parameters controlling the excess air formation.

5.2 Theory

Noble gas concentrations in natural waters are basically the result of the dissolution of atmospheric gases according to Henry's law:

\[ C_i^* = \frac{C_i^g}{K_{H,i}(T,S)} = \frac{p_i}{R \cdot T \cdot K_{H,i}(T,S)} \] (5.1)

The equilibrium concentration \( C_i^* \) of the dissolved gas \( i \) in solution is directly proportional to its atmospheric concentration \( C_i^g \). The molar atmospheric concentration is re-
lated to the partial pressure $p_i$ in the gas phase according to Dalton’s Law in which $R$ is the universal gas constant. The concentration proportionality is given by the dimensionless Henry coefficient $K_{H,i}$ which depends on temperature $T$ and salinity $S$. For the chemically inert noble gases, hence the equilibrium gas concentrations convey information about the water temperature at the time of infiltration (e. g., Stute and Schlosser, 1993).

The atomic mass of the noble gases influences their behavior in air–water partitioning (Tab. 5.1). On the one hand, the solubility of the noble gases increases with increasing atomic mass. As a result, in solubility equilibrium with the atmosphere the dissolved gas composition is enriched in the heavy gases relative to atmospheric air. On the other hand, the molecular diffusivity of the noble gases in water decreases with increasing atomic mass. This implies that any diffusive alterations of dissolved noble gas concentrations have the strongest effect on the light noble gases.

The addition of atmospheric air to solubility equilibrium concentrations yields a characteristic supersaturation pattern in which the least soluble light noble gases show the largest excess (see Tab. 2.2). The dissolved concentration of gas $i$ in case of an excess of unfractionated atmospheric air can be described as follows (e. g., Heaton and Vogel, 1981):

$$C_i(T,S,P,A_{UA}) = C_i^*(T,S,P) + A_{UA} \cdot z_i$$  \hspace{1cm} (5.2)

In this unfractionated excess air (UA) model $A_{UA}$ is the concentration of dissolved dry air in water, $z_i$ is the volume fraction of the considered gas in dry air, and $C_i^*$ is the moist air solubility equilibrium concentration at the given temperature $T$, atmospheric pressure $P$ and salinity $S$. For more information about the calculation of $C_i^*$ refer to Aeschbach-Hertig et al. (1999). Assuming that water entering the groundwater is in equilibrium with the (soil-) atmosphere, a dissolved gas excess of purely atmospheric composition can only be realized by the complete dissolution of an additional air volume.
Table 5.1: Molecular diffusivities and dimensionless Henry coefficients

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<td>1.41</td>
<td>1.84</td>
<td>10.5</td>
<td>13.4</td>
<td>16.4</td>
</tr>
<tr>
<td>Xe</td>
<td>0.774</td>
<td>1.12</td>
<td>1.47</td>
<td>5.36</td>
<td>7.29</td>
<td>9.41</td>
</tr>
<tr>
<td>(^3)He</td>
<td>5.89</td>
<td>6.33</td>
<td>7.25</td>
<td>109</td>
<td>109</td>
<td>105</td>
</tr>
<tr>
<td>(^4)He</td>
<td>5.10</td>
<td>6.30</td>
<td>7.22</td>
<td>107</td>
<td>107</td>
<td>105</td>
</tr>
<tr>
<td>(^{20})Ne</td>
<td>2.62</td>
<td>3.29</td>
<td>4.18</td>
<td>83.4</td>
<td>88.0</td>
<td>90.7</td>
</tr>
<tr>
<td>(^{22})Ne</td>
<td>2.50</td>
<td>3.14</td>
<td>3.98</td>
<td>83.2</td>
<td>88.0</td>
<td>90.5</td>
</tr>
</tbody>
</table>

D: Molecular diffusivities in water. Measured values for He, Ne, Kr and Xe were taken from Jähne et al. (1987). The diffusivity of Ar was approximated by the relationship \(D_i \sim 1/(\text{mass})^{0.5}\) using the measured values of He, Ne, Kr and Xe. Diffusivities of oxygen and nitrogen were taken from Broecker and Peng (1974).

K_H: Dimensionless Henry coefficients. They are calculated using the equilibrium concentrations assuming \(P = 1\) atm and \(S = 0\) from Weiss (1970), Weiss (1971), Weiss and Kyser (1978) and Benson and Krause (1980) for \(^3\)He, \(^4\)He, Ne, Ar and Kr, and from Clever (1979) for Xe. For \(^3\)He and \(^{22}\)Ne, the fractionation factors given by Beyerle et al. (2000) were used. The values for \(^4\)He and \(^{20}\)Ne were assumed to correspond to those of He and Ne, respectively.

Since the solubilities as well as the temperature dependency of the Henry coefficient \(K_{H,i}\) of the noble gases increase with increasing molecular weight, other possible mechanisms leading to supersaturation of dissolved gas in groundwater (mixing of water components that equilibrated at different temperatures, changes in the parameters \(T, S\) and \(P\) that define the solubility equilibrium concentration, in-situ gas production and changes in the individual partial pressures) result in dissolved elemental noble gas patterns that differ from the pure excess air signature corresponding to air injection (Tab. 2.2).
In contrast to the simple concept of complete air bubble dissolution, groundwaters sometimes show a different type of excess air composition. In this case, the gas excess exhibits a systematic, mass-dependent fractionation relative to atmospheric air which can be characterized as an increasing enrichment or decreasing depletion with increasing atomic mass. Possible mechanisms leading to such type of "fractionated excess air" are the partial diffusive degassing of an initial excess with atmospheric composition across the groundwater table (Partial re-equilibration, Stute et al., 1995b), or the equilibration of a finite water volume with a finite air volume under increased pressure (Closed-system equilibration, Aeschbach-Hertig et al., 2000).

In the first case, an initially dissolved gas excess is partially lost, either to the gas phase of the soil air across the groundwater table or during the flow process within the aquifer. As the diffusivities in water are the greater the lighter the gas is, this diffusive re-equilibration affects the light noble gases most. The partial re-equilibration model that describes the effect of a diffusively controlled gas loss considers as model parameters the amount of initially dissolved excess air $A_{PR}$ and the degree of elemental fractionation $F_{PR}$ (Stute et al., 1995; Aeschbach-Hertig et al., 1999):

$$C_i(T,S,P,A_{PR},F_{PR}) = C_i^0(T,S,P) + A_{PR} \cdot z_i \cdot e^{-\frac{F_{PR} D_L}{D_w}}$$  (5.3)

$F_{PR}$ can be interpreted as being proportional to the time during which the initial super-saturation is lost to the soil air. Fractionation of the gas excess in the PR-model is solely due to differences in molecular diffusivities between the gases.

The CE concept assumes a closed system in which a finite water volume equilibrates with a finite entrapped air volume under increased pressure. If the air volume is completely dissolved, the result is pure, unfractionated excess air. If not, the elemental compositions of both the dissolved gas and the remaining gas volume are fractionated depending on the initial air–water volume ratio and the pressure on the system. As a result, the heavy noble gases Ar, Kr and Xe are enriched in the water phase relative to
The light noble gases He and Ne. The CE model also uses two parameters to describe the fractionation process: $A_{CE}$ gives the initial amount of entrapped air, $F_{CE}$ the reduction of volume of entrapped air due to dissolution (Aeschbach-Hertig et al., 2000)

$$C_i(T,S,P,A_{CE},F_{CE}) = C_i'(T,S,P) + \frac{(1-F_{CE}) \cdot A_{CE} \cdot z_i}{1 + F_{CE} \cdot A_{CE} \cdot z_i / C_i'(T,S,P)}$$ (5.4)

The parameter $F_{CE} = v q^{-1}$ can be decomposed into the parameters $v$ describing the reduction of the entrapped air volume due to partial dissolution, and $1/q$ describing the effect of compression on the discrete gas phase. Fractionation according to the CE model does not depend on the molecular diffusivities but on the differences between the Henry coefficients of different gases and on the variations in the ratio of water volume to volume of entrapped air.

These conceptual approaches which reasonably reproduce the atmospheric noble gas abundance in natural waters (Aeschbach-Hertig et al., 1999) focus on the final state of gas exchange between entrapped air, soil air and groundwater without an explicit consideration of the processes that lead to this state. Because the models do not include microscopic kinetics and details such as the spatial and size distribution of the bubbles, they may be seen as simplified “lumped-parameter” models. Alternatively, the gas exchange and the partitioning between entrapped air bubbles and groundwater can be described in kinetic terms. Therein, the mass exchange of the five noble gases as well as of the main air constituents oxygen and nitrogen are simulated numerically for spherical air bubbles entrapped in an aquifer column. The air–water mass transfer is modeled assuming a rapid equilibration between the two phases according to Henry’s law and a water-side boundary layer gas exchange concept (Schwarzenbach et al., 1993). For one initial bubble size, the temporal change in dissolved concentration of gas $i$ is given by:

$$\frac{dC_i}{dt} = \frac{A_{int}}{V_{tot} \cdot \theta} \frac{D_i}{\delta_{eff}} (C_i - C_i^*) = \frac{A_{int}}{V_{tot} \cdot \theta} \frac{D_i}{\delta_{eff}} \left( C_i - x_i \left( \frac{p_{air} - p_w + \rho gh + 2\sigma/r}{RTK_{H,i}} \right) \right)$$ (5.5)
where $A_{\text{int}}$ is the total interface area between water and entrapped air bubbles [m$^2$], $V_{\text{tot}}$ the total volume of the considered aquifer column [m$^3$], $\theta$ is the porosity [-], $r_{\text{air-water}}$ is the ratio of the entrapped air volume and water volume [-], $D_i$ is the diffusivity of the gas in water [m$^2$.s$^{-1}$], $\delta_{\text{eff}}$ is the effective boundary layer thickness around the air bubbles [m], $C_i$ is the actual dissolved concentration and $C_i^*$ the moist air solubility equilibrium concentration of gas $i$ [mol.m$^{-3}$], $x_i$ is the mole fraction of the gas in the atmosphere [-], $p_{\text{atm}}$ is the barometric pressure [Pa], $p_w$ is the partial pressure of water vapor in the bubble [Pa], $pgh$ is the hydrostatic pressure in the water at depth $h$ [Pa], $2\sigma/r$ is the capillary pressure resulting from the curvature of the bubble surface [Pa], $\sigma$ is the surface tension [Pa.m], $R$ is the universal gas constant [Pa.m$^3$.K$^{-1}$.mol$^{-1}$], $T$ is the water temperature [K] and $K_{H,i}$ is the dimensionless Henry coefficient of gas $i$.

Initially, the water is assumed to be in solubility equilibrium with the atmosphere at given $T$, $P$ and $S$. The hydrostatic pressure at depth $h$ and the capillary pressure $2\sigma/r$ combine to an excess pressure that is exerted on a considered entrapped air bubble in the water column. Thus the bubble will dissolve until – in accordance with the actual pressure – a new equilibrium between the gas phase in the bubble and the dissolved components in the surrounding water is reached. The dissolved gas composition of this new equilibrium state is determined by the initial conditions and the solubilities of the gases. The molecular diffusivities affect the gas composition only during the transition between initial and final state. Because this transition time is rather short, the noble gas concentrations observed in groundwater samples usually reflect the composition in the final equilibrated state.

The air bubble–water mass transfer is coupled with a one-dimensional advective-diffusive transport model allowing variable and adequate discretizations in space and time. As a result, the interaction of entrapped air bubbles with flowing or stagnant water can be simulated kinetically providing insights into the temporal development of the air bubble sizes and the gas composition in both the entrapped air bubbles and in the dissolved gas phase. A more detailed description of the kinetic air bubble dissolution (KBD) model is given in Chapter 4.
5.3 Experimental

Laboratory experiments studying the formation of excess air were performed using packed sand columns. The acrylic glass columns had a length of 1 m and an inner diameter of 5.2 cm with two sampling ports at the bottom and in the middle, i.e. at 50 cm height. They were filled with clean, well-sorted quartz sand up to 80 cm above the column bottom. Quartz sand with particle sizes ranging from 0.315 mm to 0.63 mm was employed. Additionally, a coarser (particle sizes between 1.0 mm and 1.7 mm) and a finer quartz sand (particle sizes between 0.1 mm and 0.3 mm) were used.

The total porosity, the entrapped air volume after water saturation and the immobile water volume after drainage were determined gravimetrically (Tab. 5.2). For the intermediate sized quartz sand, the pore size spectrum after water saturation was measured with a low-field NMR instrument (Chen and Kinzelbach, accepted). The spectrum shows a unimodal skew pore diameter distribution between 50 μm and 800 μm with a weighted average diameter of 300 μm.

<table>
<thead>
<tr>
<th>Quartz Sand</th>
<th>Fine</th>
<th>Medium</th>
<th>Coarse</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle diameter</td>
<td>0.1 - 0.3 mm</td>
<td>0.315 - 0.63 mm</td>
<td>1.0 - 1.7 mm</td>
</tr>
<tr>
<td>Porosity</td>
<td>0.42</td>
<td>0.40</td>
<td>0.38</td>
</tr>
<tr>
<td>$V_{\text{Entrapped}} / V_{\text{Pore}}$</td>
<td>0.08</td>
<td>0.09</td>
<td>0.01</td>
</tr>
<tr>
<td>$V_{\text{Immobile}} / V_{\text{Pore}}$</td>
<td>0.76</td>
<td>0.26</td>
<td>0.22</td>
</tr>
</tbody>
</table>

$V_{\text{Entrapped}}$: Gravimetrically determined initially entrapped air volume

$V_{\text{Pore}}$: Total pore volume of a given sample volume determined gravimetrically using a quartz sand density of 2.65 g/cm³.

$V_{\text{Immobile}}$: Gravimetrically determined immobile water volume after water drainage.
Two different experimental series were performed (Fig. 5.1). In the first, the columns were water saturated from bottom to top. After this first imbibition, a constant vertical water flow with different flow velocities in the various experiments was established. The water level in the columns was kept constant at 80 cm above the column bottom. Water samples were taken from the bottom sampling port at different time intervals. The second series of experiments consisted of cyclic water level fluctuations in the columns. Each sand column was initially filled with equilibrated water to the top of the sand-filled column section. After a stagnation phase, the water was drained out of the column into a closed water vessel down to a minimal water level a few centimeters above the column bottom. In the next step, the water from the vessel was used to refill the sand column. Several experiments with various numbers of water saturation and drainage steps were performed. Samples were taken from both the bottom and the middle sampling port. The amount of water in the system during the water level fluctuations was constant. The water level changes were achieved by adjusting the height of the water vessel (Fig. 5.1).

In all experiments de-ionized water being initially in solubility equilibrium with the atmosphere was used. The equilibrium was attained by slow stirring of water in an open reservoir (25 l) for two weeks and was regularly controlled by analyses of the dissolved noble gases. In addition, noble gas concentrations in the laboratory air were measured to verify that the noble gas abundance corresponded to atmospheric composition. Biological activity in the columns was avoided by adding 4 mg/l CuSO₄ to the equilibrated water. The air temperature (20 °C ± 0.5 °C) as well as the relative humidity (90 %) was kept constant in all experiments. The atmospheric pressure in the laboratory is given by its elevation of 435 m above sea level.

For noble gas analysis, 45 ml of water were sealed-off in copper tubes under careful prevention of air contamination and degassing (Beyerle et al., 2000). The samples were analyzed for dissolved He, Ne, Ar, Kr, Xe and the isotope ratios $^{3}\text{He}/^{4}\text{He}$, $^{20}\text{Ne}/^{22}\text{Ne}$ and $^{36}\text{Ar}/^{40}\text{Ar}$ (Beyerle et al., 2000).
Experimental setup. Two different series of column experiments were performed: (1) Throughflow experiments where air-saturated water (ASW) flows through the quartz sand filled column. The water level is kept constant using a leveling reservoir LR. (2) In the water level fluctuation experiments the column was periodically water saturated and drained, thereby the total water volume in the column (closed water vessel CWV + column) is kept constant.

The interpretation of the measured noble gas concentrations in terms of the physical conditions prevailing air–water partitioning was based on the least-square optimization procedure of Aeschbach-Hertig et al. (1999) and Peeters et al. (accepted). This procedure simultaneously estimates the equilibration temperature, the dissolved concentration and the possible fractionation of excess in a sample by inverse fitting. During all experiments caution was taken to prevent access of non-atmospheric He. As the analyzed He is only of atmospheric origin, it can be included in the comprehensive interpretation of the dissolved noble gases with regard to excess air formation. In contrast, in virtually all studies of natural groundwaters, the interpretation of He concentrations in terms of recharge conditions is prevented by the presence of non-atmospheric He sources, such as radiogenic $^4$He from $\alpha$-decays in the U- and Th-series in the rock matrix.
5.4 Results

The noble gas concentrations of the column experiments are summarized in Table 5.3 and Table 5.4. To interpret the measured concentrations in terms of the physical conditions that control the soil air–water gas exchange, the least-square optimization routine NOBLE (Peeters et al., accepted) was used considering He, Ne, Ar, Kr, Xe and the isotope ratios $^{20}\text{Ne}/^{22}\text{Ne}$ and $^{36}\text{Ar}/^{40}\text{Ar}$.

Table 5.3: Noble gas concentrations of the water throughflow experiments.

<table>
<thead>
<tr>
<th>Sample</th>
<th>ST</th>
<th>FV</th>
<th>He</th>
<th>Ne</th>
<th>Ar</th>
<th>Kr</th>
<th>Xe</th>
<th>$^4\text{He}/^{20}\text{Ne}$</th>
<th>$^{20}\text{Ne}/^{22}\text{Ne}$</th>
<th>Excess Air</th>
<th>T</th>
<th>$\Delta\text{Ne}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(1)</td>
<td>(2)</td>
<td>[10^{-4}]</td>
<td>[10^{-3}]</td>
<td>[10^{-4}]</td>
<td>[10^{-4}]</td>
<td>[10^{-4}]</td>
<td>[10^{-4}]</td>
<td>[10^{-4}]</td>
<td>[10^{-4}]</td>
<td>[10^{-4}]</td>
<td></td>
</tr>
<tr>
<td>TM1</td>
<td>3</td>
<td>110</td>
<td>4.65</td>
<td>1.90</td>
<td>3.11</td>
<td>6.81</td>
<td>9.30</td>
<td>0.2709</td>
<td>0.10229</td>
<td>UA(T,A)</td>
<td>19.5 ± 0.2</td>
<td>6.2</td>
</tr>
<tr>
<td>TM2</td>
<td>4</td>
<td>20</td>
<td>4.82</td>
<td>1.98</td>
<td>3.16</td>
<td>6.87</td>
<td>9.02</td>
<td>0.2692</td>
<td>0.10188</td>
<td>CE(A,F)</td>
<td>20</td>
<td>13.6</td>
</tr>
<tr>
<td>TM3</td>
<td>4</td>
<td>40</td>
<td>4.82</td>
<td>1.98</td>
<td>3.16</td>
<td>6.87</td>
<td>9.15</td>
<td>0.2697</td>
<td>0.10225</td>
<td>UA(A)</td>
<td>20</td>
<td>11.1</td>
</tr>
<tr>
<td>TM4</td>
<td>4</td>
<td>80</td>
<td>4.67</td>
<td>1.91</td>
<td>3.07</td>
<td>6.68</td>
<td>8.94</td>
<td>0.2702</td>
<td>0.10224</td>
<td>UA(T,A)</td>
<td>19.8 ± 0.1</td>
<td>7.2</td>
</tr>
<tr>
<td>TM5</td>
<td>7</td>
<td>20</td>
<td>4.61</td>
<td>1.90</td>
<td>3.16</td>
<td>6.96</td>
<td>9.47</td>
<td>0.2689</td>
<td>0.10221</td>
<td>CE(A,F)</td>
<td>20</td>
<td>6.6</td>
</tr>
<tr>
<td>TM6</td>
<td>8</td>
<td>20</td>
<td>4.69</td>
<td>1.97</td>
<td>3.12</td>
<td>6.83</td>
<td>9.18</td>
<td>0.2632</td>
<td>0.10167</td>
<td>CE(T,A,F)</td>
<td>20.6 ± 1.1</td>
<td>11.2</td>
</tr>
<tr>
<td>TM7-I</td>
<td>8</td>
<td>10</td>
<td>4.63</td>
<td>1.92</td>
<td>3.24</td>
<td>7.07</td>
<td>9.31</td>
<td>0.2660</td>
<td>0.10228</td>
<td>CE(T,A,F)</td>
<td>19.0 ± 1.1</td>
<td>7.3</td>
</tr>
<tr>
<td>TM7-II</td>
<td>16</td>
<td>10</td>
<td>4.67</td>
<td>1.94</td>
<td>3.19</td>
<td>6.96</td>
<td>9.36</td>
<td>0.2660</td>
<td>0.10239</td>
<td>CE(T,A,F)</td>
<td>19.5 ± 1.0</td>
<td>8.6</td>
</tr>
<tr>
<td>TM7-III</td>
<td>24</td>
<td>10</td>
<td>4.82</td>
<td>1.98</td>
<td>3.14</td>
<td>6.83</td>
<td>9.07</td>
<td>0.2690</td>
<td>0.10228</td>
<td>CE(T,A,F)</td>
<td>21.0 ± 0.9</td>
<td>12.3</td>
</tr>
<tr>
<td>TM8-I</td>
<td>3</td>
<td>30</td>
<td>4.73</td>
<td>1.94</td>
<td>3.12</td>
<td>6.82</td>
<td>9.17</td>
<td>0.2700</td>
<td>0.10229</td>
<td>CE(T,A,F)</td>
<td>20.7 ± 0.9</td>
<td>9.5</td>
</tr>
<tr>
<td>TM8-II</td>
<td>6</td>
<td>30</td>
<td>4.80</td>
<td>1.96</td>
<td>3.11</td>
<td>6.74</td>
<td>9.10</td>
<td>0.2707</td>
<td>0.10210</td>
<td>CE(T,A,F)</td>
<td>20.9 ± 0.8</td>
<td>11.1</td>
</tr>
<tr>
<td>TM9-III</td>
<td>24</td>
<td>30</td>
<td>4.89</td>
<td>2.01</td>
<td>3.12</td>
<td>6.83</td>
<td>9.15</td>
<td>0.2691</td>
<td>0.10227</td>
<td>UA(T,A)</td>
<td>19.8 ± 0.2</td>
<td>12.7</td>
</tr>
<tr>
<td>TM9-I</td>
<td>2</td>
<td>50</td>
<td>4.85</td>
<td>1.98</td>
<td>3.17</td>
<td>6.97</td>
<td>9.28</td>
<td>0.2713</td>
<td>0.10234</td>
<td>CE(T,A,F)</td>
<td>21.5 ± 1.0</td>
<td>13.2</td>
</tr>
<tr>
<td>TM9-II</td>
<td>7</td>
<td>50</td>
<td>4.93</td>
<td>1.99</td>
<td>3.15</td>
<td>6.74</td>
<td>9.10</td>
<td>0.2739</td>
<td>0.10234</td>
<td>UA(T,A,F)</td>
<td>19.8 ± 0.3</td>
<td>11.6</td>
</tr>
<tr>
<td>TF10-I</td>
<td>4</td>
<td>10</td>
<td>4.86</td>
<td>1.98</td>
<td>3.20</td>
<td>6.81</td>
<td>9.28</td>
<td>0.2712</td>
<td>0.10233</td>
<td>CE(A,F)</td>
<td>20</td>
<td>13.4</td>
</tr>
<tr>
<td>TF10-II</td>
<td>8</td>
<td>10</td>
<td>4.78</td>
<td>1.99</td>
<td>3.15</td>
<td>6.81</td>
<td>9.15</td>
<td>0.2659</td>
<td>0.10190</td>
<td>CE(A,F)</td>
<td>20</td>
<td>11.7</td>
</tr>
<tr>
<td>TF10-III</td>
<td>24</td>
<td>10</td>
<td>4.95</td>
<td>2.06</td>
<td>3.14</td>
<td>6.82</td>
<td>9.33</td>
<td>0.2660</td>
<td>0.10214</td>
<td>CE(A,F)</td>
<td>20</td>
<td>15.8</td>
</tr>
<tr>
<td>TF10-IV</td>
<td>32</td>
<td>10</td>
<td>4.99</td>
<td>2.05</td>
<td>3.14</td>
<td>6.88</td>
<td>9.32</td>
<td>0.2685</td>
<td>0.10233</td>
<td>UA(T,A)</td>
<td>19.6 ± 0.4</td>
<td>15.0</td>
</tr>
<tr>
<td>TC11-I</td>
<td>8</td>
<td>10</td>
<td>4.92</td>
<td>2.03</td>
<td>3.20</td>
<td>7.00</td>
<td>9.52</td>
<td>0.2676</td>
<td>0.10202</td>
<td>CE(T,A,F)</td>
<td>19.6 ± 0.8</td>
<td>13.9</td>
</tr>
<tr>
<td>TC11-II</td>
<td>24</td>
<td>10</td>
<td>4.90</td>
<td>2.03</td>
<td>3.14</td>
<td>6.83</td>
<td>9.31</td>
<td>0.2662</td>
<td>0.10227</td>
<td>CE(A,F)</td>
<td>20</td>
<td>14.4</td>
</tr>
<tr>
<td>Equi</td>
<td>-</td>
<td>-</td>
<td>4.29</td>
<td>1.76</td>
<td>2.97</td>
<td>6.67</td>
<td>9.06</td>
<td>0.2679</td>
<td>0.10225</td>
<td>T</td>
<td>20.4 ± 0.1</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 5.3: continued

(1): T: Throughflow experiment samples:
    M: Medium-sized quartz sand (diameter 0.36-0.72 mm).
    C: Coarse quartz sand (diameter 1.0-1.7 mm).
    F: Fine quartz sand (diameter 0.1-0.3 mm).
    Equi: Average concentration of the equilibrated water.

(2): Sampling time after experiment start.

(3): Flow velocity.

(4): Analytical precision: He: 0.4%; Ne, Ar: 1%; Kr, Xe: 1.5%.

(5): Excess Air Model:
    UA: Unfractionated Excess Air model.
    CE: Closed system equilibration model (Aeschbach-Hertig et al., 2000).

(6): T predicted: Noble gas temperature as predicted by the different Excess Air models.
    If T is not included in the optimization procedure, it is set to 20 °C.

(7): Δ Ne: Ne supersaturation with regard to the determined noble gas temperature.

The noble gas temperature was usually treated as unknown model parameter in addition to the parameters A and F describing the excess air. However, if for a sample no statistically acceptable fit could be achieved, the temperature was set to 20 °C in accordance with the constant air temperature of 20 °C ± 0.5°C in the laboratory, resulting in a stronger constraint on the remaining two unknown parameters.

Samples of the stirred water reservoir over the study period confirm that this water is in atmospheric solubility equilibrium. The average air-saturated concentrations of the equilibrated water correspond to a well-constrained noble gas temperature of 20.4 ± 0.1 °C.
## Table 5.4: Noble gas concentrations of the water level fluctuation experiments.

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>Fb1-I</td>
<td>3 U</td>
<td>4.81</td>
<td>1.94</td>
<td>3.04</td>
<td>6.65</td>
<td>8.92</td>
<td>0.2737</td>
<td>0.10042</td>
<td>UA(T,A)</td>
<td>20.9 ± 0.2</td>
<td>9.9</td>
</tr>
<tr>
<td>Fm1-II</td>
<td>3 U</td>
<td>4.45</td>
<td>1.79</td>
<td>3.01</td>
<td>6.68</td>
<td>9.06</td>
<td>0.2740</td>
<td>0.10251</td>
<td>UA(T,A)</td>
<td>20.3 ± 0.2</td>
<td>1.1</td>
</tr>
<tr>
<td>Fb1-III</td>
<td>6 U-D-U</td>
<td>4.88</td>
<td>1.96</td>
<td>3.19</td>
<td>7.25</td>
<td>9.76</td>
<td>0.2756</td>
<td>0.10200</td>
<td>CE(A,F)</td>
<td>20</td>
<td>10.2</td>
</tr>
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<td>Fb1-IV</td>
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<td>1.98</td>
<td>3.05</td>
<td>6.67</td>
<td>-</td>
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<td>0.10317</td>
<td>CE(T,A,F)</td>
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<td>12.9</td>
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<td>Fb2</td>
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<td>4.79</td>
<td>1.94</td>
<td>3.06</td>
<td>6.59</td>
<td>8.89</td>
<td>0.2725</td>
<td>0.10226</td>
<td>UA(T,A)</td>
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<tr>
<td>Fb3-I</td>
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<td>4.77</td>
<td>1.95</td>
<td>3.06</td>
<td>6.67</td>
<td>9.17</td>
<td>0.2703</td>
<td>0.10211</td>
<td>UA(T,A)</td>
<td>20.4 ± 0.1</td>
<td>10.0</td>
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<td>Fb3-II</td>
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<td>4.94</td>
<td>2.01</td>
<td>3.11</td>
<td>6.83</td>
<td>9.06</td>
<td>0.2710</td>
<td>0.10238</td>
<td>UA(T,A)</td>
<td>20.0 ± 0.1</td>
<td>13.2</td>
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<tr>
<td>Fm3-III</td>
<td>4 U-D-U</td>
<td>4.43</td>
<td>1.79</td>
<td>3.10</td>
<td>6.83</td>
<td>9.02</td>
<td>0.2731</td>
<td>0.10224</td>
<td>n.</td>
<td>-</td>
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<td>Fb3-VI</td>
<td>7.5 U-D-U</td>
<td>4.80</td>
<td>1.97</td>
<td>3.07</td>
<td>6.70</td>
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<td>0.2686</td>
<td>0.10181</td>
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<td>12.4</td>
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<tr>
<td>Fb4-I</td>
<td>4.5 U</td>
<td>4.95</td>
<td>2.02</td>
<td>3.15</td>
<td>6.92</td>
<td>9.38</td>
<td>0.2700</td>
<td>0.10237</td>
<td>UA(T,A)</td>
<td>19.3 ± 0.2</td>
<td>13.2</td>
</tr>
<tr>
<td>Fb4-II</td>
<td>24 U-D-U-D-U</td>
<td>4.98</td>
<td>2.03</td>
<td>3.15</td>
<td>6.69</td>
<td>9.20</td>
<td>0.2704</td>
<td>0.10238</td>
<td>n.</td>
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<td>14.4*</td>
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<tr>
<td>Fb5</td>
<td>4 U</td>
<td>4.67</td>
<td>1.91</td>
<td>3.06</td>
<td>6.74</td>
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<td>0.2707</td>
<td>0.10232</td>
<td>UA(T,A)</td>
<td>20.0 ± 0.1</td>
<td>7.3</td>
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<tr>
<td>Fb6-p</td>
<td>4 U</td>
<td>4.71</td>
<td>1.95</td>
<td>3.08</td>
<td>6.79</td>
<td>9.13</td>
<td>0.2677</td>
<td>0.10244</td>
<td>CE(T,A,F)</td>
<td>20.6 ± 0.9</td>
<td>10.2</td>
</tr>
<tr>
<td>Fb6-pp</td>
<td>30 U-D-U</td>
<td>4.70</td>
<td>1.96</td>
<td>3.13</td>
<td>6.78</td>
<td>9.06</td>
<td>0.2552</td>
<td>0.10243</td>
<td>PR(T,A,F)</td>
<td>20.0 ± 0.3</td>
<td>10.0</td>
</tr>
<tr>
<td>Fb6-pp-III</td>
<td>52 U-D-U-D-U</td>
<td>4.61</td>
<td>1.92</td>
<td>3.08</td>
<td>6.74</td>
<td>9.18</td>
<td>0.2652</td>
<td>0.10247</td>
<td>PR(T,A,F)</td>
<td>20.0 ± 0.2</td>
<td>8.0</td>
</tr>
<tr>
<td>Fb7 Ctrl</td>
<td>65 U</td>
<td>4.92</td>
<td>2.02</td>
<td>3.11</td>
<td>6.66</td>
<td>9.10</td>
<td>0.2737</td>
<td>0.10234</td>
<td>CE(T,A)</td>
<td>21.3 ± 1.2</td>
<td>14.8</td>
</tr>
<tr>
<td>Fb8 Ctrl</td>
<td>192 U</td>
<td>4.35</td>
<td>1.87</td>
<td>3.16</td>
<td>6.92</td>
<td>9.28</td>
<td>0.2568</td>
<td>0.10245</td>
<td>PR(T,A,F)</td>
<td>19.1 ± 0.5</td>
<td>4.4</td>
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<tr>
<td>Fm9</td>
<td>7 U-D-U</td>
<td>4.39</td>
<td>1.82</td>
<td>3.08</td>
<td>6.87</td>
<td>9.12</td>
<td>0.2671</td>
<td>0.10213</td>
<td>UA(T,A)</td>
<td>19.3 ± 0.2</td>
<td>1.5</td>
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<tr>
<td>Fm10</td>
<td>24 U-D-U</td>
<td>4.34</td>
<td>1.80</td>
<td>3.04</td>
<td>6.63</td>
<td>8.95</td>
<td>0.2663</td>
<td>0.10123</td>
<td>UA(T,A)</td>
<td>20.2 ± 0.4</td>
<td>1.3</td>
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<tr>
<td>Fm11</td>
<td>24 U-D-U-D-U</td>
<td>4.37</td>
<td>1.83</td>
<td>3.08</td>
<td>6.88</td>
<td>9.00</td>
<td>0.2642</td>
<td>0.10238</td>
<td>UA(A)</td>
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<td>1.4</td>
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<tr>
<td>Fm12</td>
<td>24 U-D-U-D-U</td>
<td>4.34</td>
<td>1.82</td>
<td>3.03</td>
<td>6.65</td>
<td>8.97</td>
<td>0.2636</td>
<td>0.10227</td>
<td>UA(T,A)</td>
<td>19.9 ± 0.2</td>
<td>2.3</td>
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<tr>
<td>Fm13</td>
<td>28 U-D-U-D-U</td>
<td>4.39</td>
<td>1.82</td>
<td>3.02</td>
<td>6.65</td>
<td>8.77</td>
<td>0.2672</td>
<td>0.10238</td>
<td>UA(T,A)</td>
<td>20.3 ± 0.2</td>
<td>2.4</td>
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<tr>
<td>Fm14</td>
<td>46 U-D-U-D-U</td>
<td>4.42</td>
<td>1.83</td>
<td>3.00</td>
<td>6.68</td>
<td>8.75</td>
<td>0.2663</td>
<td>0.10194</td>
<td>UA(T,A)</td>
<td>20.5 ± 0.2</td>
<td>3.5</td>
</tr>
<tr>
<td>Fm15</td>
<td>50 U-D-U-D-U</td>
<td>4.42</td>
<td>1.84</td>
<td>3.03</td>
<td>6.80</td>
<td>8.96</td>
<td>0.2652</td>
<td>0.10309</td>
<td>UA(T,A)</td>
<td>20.0 ± 0.2</td>
<td>3.5</td>
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<tr>
<td>Equi</td>
<td>-</td>
<td>-</td>
<td>4.29</td>
<td>1.76</td>
<td>2.97</td>
<td>6.67</td>
<td>9.06</td>
<td>0.2679</td>
<td>0.10225</td>
<td>T</td>
<td>20.4 ± 0.1</td>
</tr>
</tbody>
</table>

(1): F: Fluctuation experiment samples:
m, b: Sample taken from the middle or the bottom outlet of the column.
p: Quartz sand packed in the column according to Stauffer and Dracos (1986).
pp: Quartz sand packed and not exchanged after preceding experiment.
Ctrl: Control samples
Table 5.4: continued

(2): Sampling time after experiment start.
(3): Sampling history:
   U: Up, water level rise (saturation step).
   D: Down, water level fall (drainage step).
(4): Analytical precision: He: 0.4%; Ne, Ar: 1%; Kr, Xe: 1.5%.
(5): Excess Air Model:
   UA: Unfractionated Excess Air model.
   CE: Closed system equilibration model (Aeschbach-Hertig et al., 2000).
   PR: Partial re-equilibration model (Stute et al., 1995b).
   n: no statistically acceptable model fit could be achieved.
(6): T predicted: Noble gas temperature as predicted by the different Excess Air models.
   If T is not included in the optimization procedure, it is set to 20 °C.
(7): Δ Ne: Ne supersaturation with regard to the determined noble gas temperature.

5.4.1 Water throughflow

All throughflow samples were taken from the bottom outlet of the columns where the water level was at constant height in all experiments. The results are shown in Figure 5.2a. Starting from air-saturated water ASW at 20 °C and 435 m a. s. l., all sample concentrations in the He-Ar-plot fall between the dotted excess air line defining concentrations after addition of different amounts of pure air (ASW(20°C) + Air) and the dashed line that denotes solubility equilibrium concentrations for increasing pressure (ASW(20°C) + P). To explain these increased concentrations, additional air has to be forced to dissolve in excess of atmospheric solubility equilibrium. But the excess composition deviates from pure, unfractionated excess air: the measured Ar concentrations are with respect to He too large to be explained by unfractionated excess air at the given temperature, therefore the excess composition of the throughflow samples must be fractionated. Using NOBLE, the excess patterns in 14 samples match the prognosis.
of the CE model, and 6 samples contain pure unfractionated excess air. In general, the noble gas temperatures predicted by the different gas exchange models agree well with the air temperature of the laboratory.

Within the throughflow experimental series, the influence of the flow velocity, the substrate and the timing of sampling as a function of duration of the experiment on the dissolved gas composition were investigated (Tab. 5.3). No obvious correlation of flow velocity and dissolved noble gas concentrations is observable. Although the flow velocity varied between 10 cm/h and 110 cm/h, neither the amount of supersaturation nor the relative gas composition show a functional relation to the flow velocity of the respective experiment. The size of the quartz sands also seems to have no influence on the dissolved noble gas concentrations in the samples (identified by M, C, F in Tab. 5.3).

![Figure 5.2: Measured He and Ar concentrations of (a) the throughflow experiments and (b) the water level fluctuation experiments.](image_url)
Time series samples that were taken during the same experiment at different times give evidence that the noble gas concentrations change with time elapsed since the beginning of the experiment (Fig. 5.3). The concentrations of the light noble gases He and Ne tend to increase with time whereas the concentrations of the heavy noble gases Ar and Kr tend to decrease (Tab. 5.3). Correspondingly, the CE model parameters that describe the effect of fractionation evolve with time (Tab. 5.5).

**Table 5.5:** Parameters for the CE-modeled timeseries throughflow samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>ST</th>
<th>Excess Air Model</th>
<th>$A_{CE}$ [10^{-3}]</th>
<th>$F_{CE}$</th>
<th>$q$ (T,A)</th>
<th>$v$ (T,A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>(2)</td>
<td>(3)</td>
<td>(4)</td>
<td>(5)</td>
<td>(6)</td>
<td></td>
</tr>
<tr>
<td>TM7-I</td>
<td>8</td>
<td>CE</td>
<td>91 ± 84</td>
<td>0.925 ± 0.007</td>
<td>1.066</td>
<td>0.987</td>
</tr>
<tr>
<td>TM7-II</td>
<td>16</td>
<td>CE</td>
<td>40 ± 35</td>
<td>0.906 ± 0.016</td>
<td>1.070</td>
<td>0.969</td>
</tr>
<tr>
<td>TM7-III</td>
<td>24</td>
<td>CE</td>
<td>25 ± 19</td>
<td>0.852 ± 0.025</td>
<td>1.097</td>
<td>0.934</td>
</tr>
<tr>
<td>TM8-I</td>
<td>3</td>
<td>CE</td>
<td>20 ± 18</td>
<td>0.869 ± 0.032</td>
<td>1.077</td>
<td>0.936</td>
</tr>
<tr>
<td>TM8-II</td>
<td>6</td>
<td>CE</td>
<td>15 ± 12</td>
<td>0.833 ± 0.042</td>
<td>1.085</td>
<td>0.903</td>
</tr>
<tr>
<td>TM9-I</td>
<td>2</td>
<td>CE</td>
<td>24 ± 17</td>
<td>0.824 ± 0.031</td>
<td>1.115</td>
<td>0.919</td>
</tr>
<tr>
<td>TF10-I</td>
<td>4</td>
<td>CE</td>
<td>17 ± 8</td>
<td>0.834 ± 0.021</td>
<td>1.091</td>
<td>0.910</td>
</tr>
<tr>
<td>TF10-II</td>
<td>8</td>
<td>CE</td>
<td>14 ± 6</td>
<td>0.835 ± 0.038</td>
<td>1.081</td>
<td>0.903</td>
</tr>
<tr>
<td>TF10-III</td>
<td>24</td>
<td>CE</td>
<td>7 ± 3</td>
<td>0.702 ± 0.031</td>
<td>1.096</td>
<td>0.769</td>
</tr>
<tr>
<td>TC11-I</td>
<td>8</td>
<td>CE</td>
<td>12 ± 9</td>
<td>0.790 ± 0.028</td>
<td>1.096</td>
<td>0.866</td>
</tr>
<tr>
<td>TC11-II</td>
<td>24</td>
<td>CE</td>
<td>8 ± 3</td>
<td>0.742 ± 0.022</td>
<td>1.090</td>
<td>0.810</td>
</tr>
</tbody>
</table>

(1): Throughflow experiment samples:

M: Medium-sized quartz sand (diameter 0.36-0.72 mm).
C: Coarse quartz sand (diameter 1.0-1.7 mm).
F: Fine quartz sand (diameter 0.1-0.3 mm).

(2): Sampling time after start of the experiment.

(3): Amount of initially entrapped air according to the CE-model.

(4): Degree of reduction of the amount of initially entrapped air $A$ due to partial dissolution $v$ and compression $1/q$: $F=v/q$.

(5): Relative pressure increase due to hydrostatic pressure that acts on the entrapped air. Within the 2σ niveau, $q$ can be considered as being constant in all samples.

(6): Degree of partial dissolution of the entrapped air bubbles.
In the 24 h series TM7, TF10 and TC11, decreasing values of $F_{CE}$ and the partial dissolution parameter $v$ reflect the enhanced reduction of entrapped air with increasing experiment duration. Even the amount of entrapped air $A_{CE}$ seems to decrease with time, although a conclusive interpretation is not feasible considering the relatively large errors. In the two samples from series TM8 modeled under CE assumption, the parameters $F_{CE}$ and $v$ do not give statistically significant evidence of the reduction of entrapped air.

![Graph](image-url)

**Figure 5.3:** Temporal evolution of the dissolved concentrations of (a) Ne and (b) Ar in the throughflow timeseries experiments.

In all throughflow samples, the model parameter $q$ describing the ratio of the dry gas pressure in the trapped gas to that in the free atmosphere remains constant within the $2\sigma$ level. As $q$ is a measure for the pressure acting on the entrapped air, this reflects the fact that the water level in the columns was kept at constant height during the experiments.
5.4.2 Water level fluctuations

The results from the water level fluctuation experiments are shown in Figure 5.2b. Two different groups of samples can be distinguished. The first group with relatively small He supersaturation comprises all samples that were taken from the middle outlet of the columns. The second group having significantly higher He concentrations contains all samples that were taken from the bottom outlet of the columns. Again, all predicted noble gas temperatures agree well with the air temperature in the laboratory.

The location of the sampling port and hence the hydrostatic excess pressure on the sampled water dominates the amount of dissolved gas in the water level fluctuation experiments. Independent of the number of water level fluctuations preceding the sampling, the samples from the bottom of the columns contain a larger excess (9.9%–16.2% ΔNe) than the samples from the middle in which the lower hydrostatic pressure is reflected in the smaller ΔNe values of 1.1%–4.4%.

The number of alternating saturation and drainage cycles seems at least partially to influence the excess air composition of the samples. Generally, all samples that were taken after the first water saturation of a column within an experiment can be interpreted by the UA model. After drainage and a second saturation step, the composition of the excess air in the bottom outlet samples differs from that in the middle outlet samples. The composition of the gas excess in the bottom samples is fractionated and can be explained either by the CE model or by the PR model. In contrast, samples from the middle of the columns show only a slight decrease in the dissolved He concentrations after the second saturation step. The interpretation of the noble gas patterns in these samples still obeys the UA concept. Further drainage-saturation cycles do not alter the noble gas concentrations of samples from both sampling ports any more.
Of interest are the samples Fm9 to Fm15 from the middle outlet that were taken after multiple saturation steps. The supersaturation of Ne in most of these samples is larger than that of He. Conceptually, such an excess pattern can only be explained by diffusive loss of an initially dissolved gas excess as conceptualized in the PR model. One would therefore expect these samples to be modeled correctly solely according to this diffusively controlled gas exchange approach. Nevertheless, all considered samples can satisfactorily be described by the UA model assuming no fractionation at all. The UA model fits because generally only small amounts of supersaturation are present in these samples. Considering the analytical errors, all conceptual gas exchange models can in a statistically acceptable way reproduce the noble gas patterns in the samples, even if the $^{20}\text{Ne} / ^{22}\text{Ne}$ and $^{36}\text{Ar} / ^{40}\text{Ar}$ ratios are included in the optimization procedure. Therefore any further interpretation of the dissolved noble gases in these samples in terms of air–water partitioning is hampered.

While the inverse data analysis alone does not unequivocally distinguish between the different conceptual excess air models in the samples Fm9 to Fm15, the inclusion of elemental ratios, e. g. the $^4\text{He} / ^{20}\text{Ne}$ ratio, may help to identify the mass transfer processes responsible for the observed concentration patterns. Based on the large differences in the elemental diffusivities (Tab. 5.1), diffusive changes of the gas composition affect the $^4\text{He} / ^{20}\text{Ne}$ ratio much stronger than the $^{20}\text{Ne} / ^{22}\text{Ne}$ and the $^{36}\text{Ar} / ^{40}\text{Ar}$ ratio. Figure 5.4 shows the $^4\text{He} / ^{20}\text{Ne}$ and $^{22}\text{Ne} / ^{20}\text{Ne}$ ratios of all samples from water level fluctuation experiments. For the $^{22}\text{Ne} / ^{20}\text{Ne}$ ratios, most samples arrange within error around the value of air-saturated water ASW (0.1023). The spread in the measured $^4\text{He} / ^{20}\text{Ne}$ ratios is significantly larger than in the $^{22}\text{Ne} / ^{20}\text{Ne}$ ratios. Samples in which the dissolved gas composition was altered by diffusive processes have $^4\text{He} / ^{20}\text{Ne}$ ratios smaller than that of air-saturated water ASW at 20 °C (0.2672). Samples with a CE- or UA-type excess air composition fall within the range between ASW and the ratio of atmospheric air (0.3185).

Interestingly, all samples taken from the middle outlet after multiple saturation steps have $^4\text{He} / ^{20}\text{Ne}$ ratios smaller than ASW at 20 °C (Tab. 5.4). This seems to indicate that these samples were affected by diffusive gas loss prior to sampling. As the $^4\text{He} / ^{20}\text{Ne}$
Results

ratios of the two samples from the middle outlet taken after the first water saturation show no evidence of a diffusive alteration in their gas composition, the gas loss present in the other samples apparently requires a drainage step before sampling.

![Diagram](image)

**Figure 5.4:** $^{4}\text{He}/^{20}\text{Ne}$ versus $^{22}\text{Ne}/^{20}\text{Ne}$ isotopic ratios of the water level fluctuation samples. All samples with an excess air composition according to the CE or the UA model have $^{4}\text{He}/^{20}\text{Ne}$ ratios greater than air-saturated water at 20 °C (0.2672). Samples with a PR-type fractionation of the noble gas composition have $^{4}\text{He}/^{20}\text{Ne}$ ratios smaller than 0.2672 as expected from the underlying diffusively controlled gas exchange concept. In addition, all water level fluctuation samples taken from the middle column outlet after two or more water saturation steps also show $^{4}\text{He}/^{20}\text{Ne}$ ratios smaller than 0.2672.
5.5 Discussion

The reproducible generation of excess air in laboratory experiments succeeded. By simulating the natural processes of infiltration (water throughflow) and groundwater level changes (water level fluctuations), significant supersaturations could be generated in the columns. The amounts of dissolved gas excess found in our experiments are in the same order of magnitude as in shallow aquifers with periodic groundwater level fluctuations of about 1 m (Beyerle et al., 1999). The formation of excess in our experiments is related to either the complete or the partial dissolution of entrapped air bubbles. As in all porous media, air bubbles are entrapped whenever the quartz sand in the columns is water saturated. Although direct methods for the detection of entrapped air are scarce, the weight difference between a column after water level rise and the completely water saturated situation, achievable by CO₂-flushing prior to water filling, evidence the presence of entrapped air. Due to the water overload, the air bubbles are subject to mass transfer with the surrounding water immediately after their entrapment. Therefore, one of the most prominent parameters influencing the amount of excess air is the hydrostatic pressure that can act on the entrapped air bubbles – an aspect that is also identifiable in groundwater samples (Aeschbach-Hertig et al., 2001). Regarding the composition of the dissolved gas excess, our experiments reveal various physical processes that constrain the formation and composition of the excess air component.

5.5.1 Water throughflow experiments

All throughflow samples have noble gas supersaturations in accordance with the prevailing hydraulic overload. For the CE-modeled samples, this overload is reflected in the \( q \) parameter (Aeschbach-Hertig et al., 2001). Although \( q \) is approximately constant within each single throughflow experiment, a random variation of \( q \) between 1.115 and 1.066 is evident considering the different experiments (Tab. 5.5). Similarly, the concentrations of the light noble gases, in particular of He, that reacts most sensitively to
excess air and hence manifests the hydraulic excess pressure, show a random spread (Fig. 5.2a, for He). Two reasons may explain this distribution: First, an inherent variability of the sand filling process and of the water saturation procedure is present. Although all experiments were performed completely in the same way, the assumption that each column had exactly the same porosity, the same amount of entrapped air and the same bubble size distribution of entrapped air is not realistic (Williams and Oostrom, 2000). Second, the sampling procedure does not allow collecting water from an exactly defined position within the column. The withdrawn water volume rather represents a vertical column segment of 10 ± 5 cm. Both aspects may lead to variations in the total amount of excess air that is documented in the light noble gas concentrations. But although the amount of excess air varies, the composition of the excess air is surprisingly constant as expressed by the CE-type fractionation of most samples.

To gain a better understanding of the underlying physical processes responsible for the formation of excess air in the throughflow experiments, the KBD model was applied to simulate the dissolution of air bubbles in a soil column with advective water flow. The KBD model was run with the following settings: Average diameter of entrapped air bubbles: 0.3 mm, ratio of entrapped air volume and water volume: 0.09, porosity: 0.4, column height: 80 cm, specific discharge: 10 cm/h, vertical discretization: 5 cm, temporal discretization: 10 s, water temperature: 20 °C, barometric pressure: 97425 Pa. These settings correspond to the throughflow experiments with intermediate-sized quartz sand considering only the most frequent size of entrapped air bubbles. The simulation result is shown in Figure 5.5.

Bubble radii in 4 depth classes are displayed with increasing time in Figure 5.5a. All entrapped bubbles are completely dissolved. The bubble extinction occurs first in the uppermost vertical box, followed by dissolution in the level below and so forth. This characteristic evolution is the result of the continuous vertical water flow in the column in which the uppermost box is refilled with water equilibrated at atmospheric pressure enhancing the effectiveness of the dissolution. The time scale for the dissolution of all entrapped air is in the order of 6 days.
Figure 5.5: Results for 4 depth levels from a run of the KBD model with parameters defined by the throughflow experiments. (a) Bubble radii with time. All air bubbles dissolve completely, starting in the uppermost vertical box. The time scale for the complete dissolution is approximately 6 days. (b) Relative dissolved noble gas composition with time.

Figure 5.5b shows the modeled relative changes in the dissolved noble gas concentrations at the column bottom. Starting from atmospheric solubility equilibrium, the concentrations are increasing nearly immediately after the simulation begins as a result of sudden application of pressure to the entrapped bubbles. After this first spike that is a result of the conceptualization of initial conditions within the KBD model, the relative noble gas composition evolves differently for the light noble gases and the heavy noble gases. In a first phase, the relative He and Ne concentrations increase whereas Ar, Kr and Xe relatively decrease. The dissolution process in this period is characterized by the adaptation of mass transfer to the hydraulic excess pressure. In the second, quasi steady-state period the amount of dissolved gas in each time step yields nearly constant dissolved noble gas concentrations. This plateau-like concentrations are reached the faster the more soluble the gas. On average, quasi steady-state conditions in the relative gas composition are reached within 30 hours. After the complete dissolution of all air
Discussion

bubbles, the noble gas concentrations are reaching again the atmospheric solubility equilibrium concentration of the water inflow.

If the gas compositions resulting from this KBD model simulation are interpreted with the bulk gas exchange concepts, the first, non-steady phase can be described by the CE model whereas the quasi steady state phase matches the UA approach. The modeled results agree well with the results from the time series experiments: Almost all samples from experiments with small flow velocities (< 30 cm/h) that were taken within 24 h after the start of the respective experiment have a noble gas composition that is described by a CE-type noble gas composition. These samples apparently stem from the first non-steady-state dissolution phase. In contrast, the sample TF10-IV that was taken after 32 h has a purely atmospheric noble gas excess suggesting that the quasi steady-state phase has already been reached.

Figure 5.6 compares the results of the numerical simulation with the measured values of the time series from experiment TM7. The samples show the same temporal trend in the relative gas composition as predicted by the KBD model: The light noble gases He and Ne are increasing whereas Ar, Kr and Xe are decreasing. The temporal delay of the measured data in comparison to the model results most probably results from the range in the bubble sizes present in the column experiments. KBD simulations with several bubble size classes showed that for each given depth only one bubble size can be stable with respect to the prevailing pressure. Therefore a rearrangement within the bubble sizes occurs immediately after the start of the simulation leading to only one respective bubble size persisting at each depth. As a result, the timescale for the dissolution of all entrapped air is prolonged compared to a single bubble size class. Besides the timing, the model prognosis for the concentrations is in a good agreement with the measured data if the analytical uncertainty is considered. Only for the relative He concentrations larger discrepancies are evident.
Figure 5.6: Detail of the numerical simulation of the throughflow experiments including the measured results of experimental series TM7.

Numerical simulations with larger flow velocities show that the general concentration evolution is independent of the flow velocity. However, faster advective flow forces faster complete bubble dissolution and accelerates the transition from the initial non-steady state phase to the quasi steady-state situation. Therefore, as expected from the numerical simulation, in the experiments with flow velocities $\geq 30$ cm/h, the quasi steady-state condition with constant relative elemental abundance is reached considerably faster (Sample TM1, TM3, TM4 and TM9-II).
5.5.2 Water level fluctuation experiments

As in the water throughflow experiments, the hydrostatic pressure is the dominating parameter influencing the total amount of dissolved entrapped air. Samples from the middle outlet of the columns like Fm1-II and Fm3-III have significantly smaller supersaturations, especially in case of the light noble gases He and Ne, than the samples from the bottom column outlet. The differences in the amounts of excess air between the two sampling ports as well as the absolute magnitude of the supersaturations agree well with the predictions by the CE and UA model respectively. The dissolved gas composition of most of the samples can be predicted correctly.

![Figure 5.7: Results from a KBD model simulation with parameters defined by the water level fluctuation experiments after the first water saturation (no advective water flow). (a) Bubble radii with time. The entrapped air bubbles do not dissolved completely. (b) Dissolved noble gas concentrations with time. The better soluble the gas, the smaller is the relative increase in the dissolved concentrations.](image-url)
To analyze the experimental results and identify the underlying physical processes, the KBD model was used to simulate the first saturation step, using the same initial parameters as for the throughflow simulation except that the advective water flow was set to zero. The results of the simulation are shown in Figure 5.7. As expected from the experiment design, the entrapped air bubbles dissolve only partially as the hydrostatic excess pressure alone is too small to force the entrapped air bubbles to dissolve completely. The entrapped air bubbles are partially dissolved until a new equilibrium is reached between the remaining entrapped air bubbles and the surrounding water. As shown in Figure 5.7a, it takes about ten minutes to establish equilibrium conditions. The experimental data support the modeled results. Sample Fb3-I taken 5 min. after the start of the experiment has not yet reached the final equilibrium conditions since the dissolved concentrations are still increasing towards the sample Fb3-II that was taken after 4 h. Regarding the elemental composition, a temporal discrepancy between the simulation and the measured data exists. Similarly to the throughflow experiments, the distribution of the entrapped air volume in a range of bubble sizes delays the partial dissolution process and the attainment of the new steady-state condition. Since very small entrapped bubbles can be completely dissolved under closed-system equilibration conditions as well, the bottom samples taken within 4 hours after the beginning of the experiment still show an unfractionated gas excess composition. Nevertheless, a major portion of the excess air is already detectable after a few minutes in the experiments, which is in agreement with the results of the numerical simulation. The equilibration time increases generally with depth, i.e. with hydrostatic pressure, because according to Henry’s law the maximum amount of gas that can be solved increases with increasing pressure.

Besides the hydrostatic pressure, the available amount of entrapped air and the entrapped bubble sizes seem to affect crucially the amount and the composition of excess air. Sample Fbp5 was taken in an experiment in which the quartz sand was packed to reach the most dense filling using the technique of Stauffer and Dracos, 1986. In result, the porosity and hence the total amount of entrapped air in this column is smaller than in the other experiments. The measured dissolved concentrations of this packed column
Discussion

are significantly lower, especially in the case of the light noble gases He and Ne, than in the bottom samples from other experiments. This suggests that the entrapped air volume available for dissolution in this experiment was smaller than in the unpacked columns. The porosity and hence the total amount of entrapped air therefore are important factors controlling the total amount of dissolved excess air.

The following Fbpw6 series was conducted using the same column without replacing the sand. Initially the sand in this series was therefore not dry, but contained a residual amount of adsorbed water. In contrast to all other samples that were taken after the first water saturation, the sample Fbpw6-I has a fractionated gas excess pattern in accordance with the CE approach. This documents that in the first saturation step of series Fbpw6 the smallest pores are occupied by immobile water and therefore not available for air entrapment. As a result, the entrapped air bubble size distribution is loosing its smallest sizes. Only larger air bubbles are entrapped which dissolve only partially under the given pressure conditions. The arising concentration pattern thus corresponds to the CE concept. In contrast, the usual experimental procedure using dry sand allows air bubbles to be entrapped in the smallest pores during the first water saturation. These very small air bubbles can be completely dissolved, leading to a gas excess with pure atmospheric composition soon after the start of the experiment (e.g., Fb1-I, Fb2, Fb3-I).

From the experimental procedure and the application of the conceptual gas exchange models, it still cannot be explained why after the first water saturation step any further imbibition has no obvious influence on the dissolved gas composition at the column bottom. Furthermore, it is not clear why these further water saturation steps seem to produce a PR-type fractionation in the middle outlet samples. To explain the latter, a diffusive gas loss across either the water level in the column or through the acrylic column walls can be assumed. Considering the effective diffusion coefficients of the gases in a water-filled porous medium, which are approximately one order smaller than those in pure water, a solely diffusive gas transport from the middle of the column towards the water level cannot at all alter the gas composition on the time scale of our experi-
ments. To test whether gas losses through the column wall are possible on the relevant temporal scale, we measured the dissolved noble gas content in two control samples, Fb7 Ctrl and Fb8 Ctrl. The gas composition in sample Fb7 Ctrl taken 65 hours after a first water saturation step shows no sign of diffusive gas loss. In contrast, sample Fb8 Ctrl taken after a 192 hours stagnation period is characteristically fractionated: The light noble gases are depleted and the heavy noble gases are enriched, consequently the noble gas excess can only be explained by the PR-approach. Thus, diffusive gas losses through the column walls seem to occur on larger time scales, but for the time needed to perform our experiments, this kind of long-term diffusive loss is negligible.

To understand the processes leading to the observed noble gas pattern after multiple water saturation steps, we analyzed the dissolution kinetics employing the KBD model (Fig. 5.8). Considering no-flow conditions, a simplified water level fluctuation approach was simulated: After the first water saturation, we assume that all the water is virtually withdrawn from the column and mixed completely. As a result, the concentrations in the water become the average of all concentrations from different column depths. This average approximately corresponds to the concentration in the geometric center of the column. In the second water saturation step, the column is refilled with this water, which is of average supersaturation with respect to atmospheric solubility equilibrium. Air bubbles consisting of pure atmospheric air are entrapped in this second step and equilibrate with the already supersaturated water component. The resulting new equilibrium concentrations in the water depend strongly on the applied hydrostatic pressure and on the gas solubility.

At the bottom of the column, the concentrations are hardly different from those of the first saturation step. The averaged dissolved gas excess applied in the second step is still smaller than the expected equilibrium concentrations for the given hydrostatic pressure at the bottom. Thus, in the lower part of the column, the dissolved concentrations still increase towards the newly established equilibrium condition as shown in Figure 5.8a for He.
Figure 5.8: Noble gas composition for a simplified water level fluctuation approach modeled by the KBD model after refilling a soil column with an averaged supersaturated water. (a) The dissolved He concentrations for the lower part of the column still increase. In contrast, in the upper column section the He concentrations decrease as a result of the relatively smaller hydrostatic pressure, which implies that the mass flux in this upper section goes from the water into the entrapped air bubbles. (b) Relative changes in the amounts of the dissolved noble gases. The decrease in the upper column section and the increase in the lower part of the column are controlled by the gas solubilities. The relative change is the more effective, the lower the solubility of the gas is. The resulting gas excess pattern for the column bottom can be described by the CE approach, whereas the noble gas composition from the upper section with its characteristic decrease in the light noble gases resembles a diffusively controlled gas loss following the PR concept. Nevertheless, the resulting patterns are the result of a solubility-controlled re-solution from a dissolved supersaturation into entrapped air bubbles with atmospheric composition.

With decreasing hydrostatic pressure in the upper part of the column, the maximum amount of gas that can be dissolved in equilibrium with the entrapped air decreases. As a result, for smaller hydrostatic pressures the averaged gas excess in the applied water is already larger than expected from the new equilibrium with the entrapped air. In this case, the mass transfer is from water into the entrapped air bubbles as depicted for He in Figure 5.8a. The effectiveness of the dissolved gas composition to attain the new equilibrium conditions in the column is controlled by the solubility of the gases. Figure
5.8b shows the relative changes in the amount of dissolved gas at the bottom and at the middle outlet of the column. The increase in the amount of dissolved gas at the bottom as well as the decrease in the middle outlet section of the column is the larger, the smaller the solubility of the gas. As a result, we find a new equilibrium concentration pattern for the middle column outlet that is characterized by a depletion of the light noble gases compared to the heavier ones, whereas at the column bottom the new equilibrium is nearly identical to that after the first saturation. The corresponding excess patterns are shown in Figure 5.8. As expected, the composition of the dissolved gas excess at the column bottom is in agreement with the CE model. In contrast, in the middle outlet we find the He supersaturation smaller than that of Ne, and the Ne excess smaller than that of Ar. Such a dissolved concentration pattern can conceptually only be explained by the PR approach. However, the shown result originates not from a diffusive loss of an initially dissolved gas excess across the water table, but from the differences in the solubilities of the gases that lead to a selective re-solution of a dissolved excess into entrapped air bubbles.

If we proceed, further drainage-wetting steps have virtually no additional influence on the noble gas abundance in the column. Since the processes leading to the final dissolved concentrations in the second saturation step are identical to those in all following saturation steps, also the attained equilibrium concentrations should be the same and no further changes in the dissolved gas composition can be expected from continued water saturation.

In conclusion, the numerical analysis allows to understand on a sound physical basis why after the second saturation step the dissolved noble gas composition of the middle outlet samples tends towards a pseudo-diffusive PR-type fractionation whereas the composition of the bottom outlet samples do not show such a evolution, and why any further saturation steps have no effect on the composition and on the amount of the dissolved noble gases.
5.5.3 Identification of relevant parameters in the formation of excess air

Combining the results from both experimental investigations and numerical simulations of the entrapped air dissolution, we are able to identify the following physical constraints controlling the formation of excess air in quasi-saturated porous media:

1. Pressure: The hydrostatic pressure exerted on the entrapped air is the dominating parameter responsible for the total amount of dissolved air. The hydrostatic pressure together with the capillary pressure of the bubble surface force a new equilibrium condition between the entrapped bubbles and their surrounding water. In accordance with Henry’s law, the noble gas excess increases with growing total pressure. Furthermore, the hydrostatic pressure can prevent the diffusive degassing of an initial dissolved gas excess. This explains why in groundwater studies samples with a partial re-equilibration signature can rarely be found. Since such studies aim to obtain the initial excess air composition, usually water from a certain depth within the aquifer is sampled. The hydrostatic pressure at that depth hinders the water to re-equilibrate to atmospheric conditions.

2. Flow regime: A predominantly vertical advective flow regime favors the complete dissolution of entrapped air bubbles and hence the formation of a dissolved gas excess with a composition that falls in the range between closed-system equilibration (first dissolution phase) and unfractionated excess air (second phase until complete dissolution). In stagnating waters, only closed-system equilibration conditions occur. Switching the flow regime between flow and no-flow conditions can lead to secondary gas exchange processes within the considered water column leading to a depletion of the light noble gases relative to the heavier ones.
The flow velocity defines the timescale of the entrapped air dissolution process. As documented by the throughflow experiments, the dissolved gas composition depends on the sampling time in relation to the flow velocity.

3. Total volume of initially entrapped air: The initially entrapped air volume limits the maximum possible amount of excess air being generated. Whereas for no-flow conditions the entrapped air volume is usually not completely dissolved, complete dissolution of entrapped air seems to occur only on larger timescales and only under continuous vertical flow conditions. Soil parameters, such as the porosity and particle size distribution, influence the total available volume of entrapped air and thus affect the amount of excess air.

4. Entrapped air bubble size: The size distribution of the entrapped air bubbles influences the excess air composition. Very small bubbles are much more likely subject to complete dissolution, resulting in unfractionated excess air. Larger bubbles have – depending on the flow velocity – significantly larger lifetimes and may therefore not be completely dissolved at all under natural flow conditions in aquifers. This situation favors the formation of fractionated excess air.

5. Initial composition of the dissolved gases: The initial composition of the dissolved gas is important for the mass transfer between entrapped air and water. If infiltrating water already contains noble gases in excess as simulated by our imbibition-drainage experiments, and equilibrates with entrapped air bubbles of purely atmospheric composition, the heavy noble gases are significantly enriched compared to the light ones. Although the gas composition seems to resemble fractionation due to diffusive loss of an initial gas excess across the water table, it is the result of a new equilibrium state between initially supersaturated water and entrapped air and thus controlled by the gas solubilities.
6. Initial gas composition of entrapped air: Although not directly evidenced in our experiments, the initial composition of the gas in the entrapped air bubbles can also play a role in the composition of the resulting excess air. While usually air-like gas abundances are assumed for entrapped air, it can be shown that the equilibration of a water volume in atmospheric solubility equilibrium with an entrapped gas phase that was preconditioned by a temporary partial dissolution step may lead to a fractionated excess air pattern in water comparable with the PR-approach.

5.6 Conclusions

In the present study the reproducible generation of excess air under defined, near natural boundary conditions in column experiments was successfully realized. The degree of gas supersaturation range between 1.4 % ΔNe to 16.2 % ΔNe depending on the chosen experimental design. Using a combined approach of experimental investigations and modeling of gas exchange concepts and kinetics of air bubble dissolution in soil columns, excess air formation could be verified in a reproducible manner for the first time. The partial or the complete dissolution of entrapped air bubbles under quasi-saturated conditions is identified to be the mechanism that is responsible for the formation of excess air. The dominating parameter responsible for the total amount of dissolved air is the hydrostatic pressure acting on the entrapped air bubbles. It governs the equilibrium between entrapped air and water in the quasi-saturated zone. Moreover, the total amount of entrapped air available for dissolution has an influence on the resulting amount of excess air. The composition of the generated excess air component is controlled by a number of factors: The water flow regime, the entrapped air bubble size distribution and the initially dissolved gas composition are reflected in the composition of the dissolved gas excess in a quasi-saturated porous medium.
Acknowledgements

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Chapter 6

Long-term observation of dissolved noble gases in a large sand filter with advective flow regime

6.1 Introduction

In natural soils, the entrapment of air bubbles during a rise in the groundwater table or surface water infiltration is a process that is physically very difficult to define in detail. Due to substrate heterogeneity and the complex structure of the soil pore space, small-scale variations in the amount of entrapped air and in the size distribution of the entrapped air bubbles are very likely to occur. Whilst the generation of excess air in quasi-saturated media from entrapped air bubbles seems to be an averaging process that smoothes out such small-scale variations, the aspect of scale and its relationship to the different mechanisms involved in the formation of excess air may be reflected in the excess air composition on different temporal and spatial scales. Under laboratory conditions, the excess air formation was successfully investigated in defined column experiments (Chapter 5). However, the question of how representative the results derived from the columns are in larger scale environments still has to be examined carefully. A larger scale confirmation of the previous findings is therefore desirable and necessary to evaluate the applicability of the developed physical concept of bubble-mediated gas exchange in “real-world” dimensions. Bringing a quartz sand filter used in the purification of drinking water back into operation after cleaning represented a unique opportunity to perform such an investigation in a relatively simple system on
larger temporal and spatial scales. Long-term observations of the dissolved gas composition in the sand filter with a controlled vertically advective flow regime yielded upscaled information about the formation of excess air in porous media.

6.2 Experimental

6.2.1 The slow filter

The Wasserversorgung Zürich (WVZ), the drinking water supply utility of the city of Zurich, provides the drinking water for more than 400000 people in the Zurich region. Of the $6.3 \times 10^7$ m$^3$ of drinking water produced each year, about two-thirds originates from the hypolimnion of Lake Zurich, and one third is groundwater. The relatively large proportion of surface water in the raw water requires a combined treatment procedure consisting of complementary mechanical/biological and chemical methods. In their raw water treatment plants, the WVZ employs a two-stage mechanical filtration, the first of which is a preliminary rapid filtration in a backflushing sand filter layer. The periodic turbulent backflushing of this filter sand with water provides on the one hand the oxygen required to maintain the biochemical activity in the filter, and on the other hand it serves to clean the sand.

After pre-filtration, the water is slow-filtered in large sand beds (Fig. 6.1). At the end of this second filtration stage, the cleaned water is fed into the WVZ water supply network of. Since the sand filling in the slow filters cannot be backflushed, the sand has to be cleaned after being in operation for 10 to 12 years. For this purpose the sand is completely removed from its bed, cleaned, washed, and then used to refill the filter.
The slow filters are built on a base of filtering bricks at the bottom that collect the filtered water (Fig. 6.2). The bricks are covered by a thin layer of gravel that serves the function of stabilizing the overlying sand layer, which consists of 1 m of medium-sized quartz sand that serves as the actual filter material. The filter sand is submerged in water supplied at the top of the filter producing an excess hydraulic head of at most 90 cm with respect to the filter surface. In the usual operation mode, this hydraulic head varies between 15 and 35 cm. The characteristics of the slow filter are summarized in Table 6.1.

Due to the pre-treatment of the water and the admixture of groundwater to the lake water, the raw water entering the slow filter is not in solubility equilibrium with the atmosphere but is already supersaturated and contains an amount of dissolved excess air. Before the slow filter was brought back into operation after the cleaning process, the dissolved gas composition in the water flowing into several other slow filters at the Moos water treatment plant was analyzed to determine whether or not the composition and the degree of supersaturation in the inflowing water remains constant. These preliminary investigations showed a relatively constant atmospheric gas excess of approximately 8% ΔNe and an elemental pattern corresponding to that of the atmosphere.
6.2.2 The filter re-operation

In June 2000, one of the fourteen slow filters in the Moos raw water treatment plant was put into operation again after the sand had been cleaned and the filter refilled. After having been refilled with fresh sand, the filter was initially flushed with normal drinking water for one day. After this preliminary flushing, the filter sand was drained for 2 hours. In the next stage, the wet sand in the filter was saturated from bottom to top with rapidly filtered raw water. When the excess hydraulic head reached 30 cm above the filter surface, the slow filter system entered a cleaning mode. In this phase the outflow of the filter is pumped to the wastewater drain. The cleaning mode ran for
two weeks until the hygienic parameters in the outflow water met the relevant drinking water specifications. Afterwards, when the system is operating regularly, the water collected at the bottom of the filter is fed into the water supply network. To achieve the required discharge from the slow filter, the change in the mode of operation was accompanied by a slight increase in the specific flow rate.

### Table 6.1: Characteristics of the slow filter, Zurich Drinking Water Supply

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total filter depth</td>
<td>1.3 m</td>
</tr>
<tr>
<td>Filter surface area</td>
<td>1120 m²</td>
</tr>
<tr>
<td>Depth quartz sand layer</td>
<td>1 m</td>
</tr>
<tr>
<td>Depth gravel layer</td>
<td>0.3 m</td>
</tr>
<tr>
<td>Quartz sand size</td>
<td>0.2 – 2 mm</td>
</tr>
<tr>
<td>Porosity</td>
<td>0.4</td>
</tr>
<tr>
<td>Specific discharge</td>
<td>11 cm·h⁻¹ cleaning mode</td>
</tr>
<tr>
<td></td>
<td>14 cm·h⁻¹ operation mode</td>
</tr>
<tr>
<td>Water temperature</td>
<td>6 °C – 8 °C</td>
</tr>
<tr>
<td>Hydraulic head above filter surface</td>
<td>15 – 35 cm</td>
</tr>
<tr>
<td>Elevation</td>
<td>450 m a.s.l.</td>
</tr>
<tr>
<td>Salinity</td>
<td>&lt; 1 %</td>
</tr>
<tr>
<td>Dissolved concentrations in the water inflow</td>
<td>C_{equi} + 8·10⁻⁴ cm³ air / gr water (approximately constant with time)</td>
</tr>
</tbody>
</table>

During the first imbition of raw water, air bubbles are trapped in the wet quartz sand. As a result of the subsequent vertical water flow, these entrapped air bubbles are expected to dissolve completely with time. The progressive dissolution of the entrapped gas phase should consequently result in a dissolved gas excess. To test this assumption, the gas composition in the filter was monitored regularly for six months. Water samples were taken from the outflow of the sand filter and from the water inflow water. The samples were analyzed for the dissolved noble gases He, Ne, Ar, Kr and Xe according to the procedure described by Beyerle et al. (2000).
Except for its spatial and temporal dimensions, the geometry of the slow filter investigated is nearly identical to that of the water throughflow experiments performed in the small-scale laboratory column experiments (Chapter 5). Hence, a comparison between the results of the column experiments and the dissolved gas concentrations in the outflow of the filter may provide useful information on the scale dependence of the formation of excess air in porous media.

### 6.3 Results

Measured noble gas concentrations for the first six months after the WVZ slow filter had been brought back into operation are given in Table 6.2 (filter outflow) and in Table 6.3 (water inflow). From the results of the laboratory column experiments, a rather rapid change in dissolved gas concentrations in response to the beginning dissolution of the entrapped air was expected. Sampling was therefore relatively frequent – at almost daily intervals – during the first phase after startup. In the later parts of the study, the sampling intervals were successively increased.

An overview of the temporal evolution of the concentrations of dissolved noble gases is given in Figure 6.3. The concentrations in the water inflow are referenced to the first measured concentration in the inflow ($C_{\text{in},t} / C_{\text{in},0}$), whereas the outflow samples are related to their corresponding inflow concentration at each time ($C_{\text{out},t} / C_{\text{in},t}$), applying a linear interpolation between the dates for which measured concentrations in the inflow are available.

In the water inflow, the concentrations remained relatively constant throughout the entire study period, although short, transient fluctuations are present in the concentration profiles (Fig. 6.3a). The maximum observable concentration variation in the inflow is ± 4 % of the initial concentration.
Table 6.2: Measured noble gas concentrations in the outflow of the slow filter.

<table>
<thead>
<tr>
<th>Sample</th>
<th>SD</th>
<th>ST</th>
<th>T</th>
<th>He 10⁴</th>
<th>Ne 10⁷</th>
<th>Ar 10⁹</th>
<th>Kr 10¹</th>
<th>Xe 10¹</th>
<th>²⁰Ne²³Ne</th>
<th>Excess Air Model</th>
<th>T</th>
<th>ΔNe</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[d.m.y]</td>
<td>[d]</td>
<td>[°C]</td>
<td>[cm³ STP/g H₂O]</td>
<td>[-]</td>
<td>[°C]</td>
<td>[%]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OF1</td>
<td>5.60</td>
<td>0</td>
<td>7.7</td>
<td>4.84</td>
<td>2.05</td>
<td>3.90</td>
<td>9.32</td>
<td>13.77</td>
<td>0.2608</td>
<td>CE(T,A,F)</td>
<td>8.0±0.2</td>
<td>3.9</td>
</tr>
<tr>
<td>OF2</td>
<td>6.60</td>
<td>1.2</td>
<td>7.8</td>
<td>5.63</td>
<td>2.37</td>
<td>4.06</td>
<td>9.54</td>
<td>13.91</td>
<td>0.2629</td>
<td>UA(T,A)</td>
<td>8.0±0.4</td>
<td>19.8</td>
</tr>
<tr>
<td>OF3</td>
<td>6.60</td>
<td>1.8</td>
<td>7.8</td>
<td>5.83</td>
<td>2.43</td>
<td>4.38</td>
<td>10.49</td>
<td>14.10</td>
<td>0.2646</td>
<td>CE(A,F)</td>
<td>7.8</td>
<td>22.7</td>
</tr>
<tr>
<td>OF4</td>
<td>6.60</td>
<td>1.9</td>
<td>7.8</td>
<td>5.8</td>
<td>2.43</td>
<td>4.22</td>
<td>10.06</td>
<td>14.52</td>
<td>0.2633</td>
<td>CE(A,F)</td>
<td>7.8</td>
<td>23.1</td>
</tr>
<tr>
<td>OF5</td>
<td>7.60</td>
<td>2.3</td>
<td>7.8</td>
<td>5.94</td>
<td>2.52</td>
<td>4.45</td>
<td>10.16</td>
<td>14.35</td>
<td>0.2612</td>
<td>CE(T,A,F)</td>
<td>7.7±0.8</td>
<td>27.3</td>
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<tr>
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<td>9.60</td>
<td>4</td>
<td>7.6</td>
<td>5.98</td>
<td>2.51</td>
<td>4.36</td>
<td>10.16</td>
<td>14.91</td>
<td>0.2636</td>
<td>CE(A,F)</td>
<td>7.6</td>
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<tr>
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<td>11.60</td>
<td>6</td>
<td>7.6</td>
<td>6.05</td>
<td>2.52</td>
<td>4.38</td>
<td>10.10</td>
<td>14.60</td>
<td>0.2644</td>
<td>n.</td>
<td>n.</td>
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<tr>
<td>OF8</td>
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<td>8</td>
<td>7.8</td>
<td>5.96</td>
<td>2.54</td>
<td>4.34</td>
<td>10.04</td>
<td>14.20</td>
<td>0.2598</td>
<td>UA(T,A)</td>
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<tr>
<td>OF9</td>
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<td>11</td>
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<td>6.00</td>
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<td>n.</td>
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<tr>
<td>OF10</td>
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<td>12</td>
<td>7.8</td>
<td>5.26</td>
<td>2.30</td>
<td>4.23</td>
<td>10.02</td>
<td>14.24</td>
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<td>UA(T,A)</td>
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<tr>
<td>OF11</td>
<td>17.60</td>
<td>12.5</td>
<td>7.8</td>
<td>4.93</td>
<td>2.09</td>
<td>4.31</td>
<td>10.08</td>
<td>14.53</td>
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<td>n.</td>
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<td>13.5</td>
<td>8.0</td>
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<td>2.08</td>
<td>4.34</td>
<td>10.06</td>
<td>14.74</td>
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<td>n.</td>
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<tr>
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<td>21.60</td>
<td>16</td>
<td>7.4</td>
<td>4.66</td>
<td>2.09</td>
<td>4.29</td>
<td>10.13</td>
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<td>0.2473</td>
<td>n.</td>
<td>n.</td>
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<td>7.6</td>
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<td>4.24</td>
<td>10.08</td>
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<td>n.</td>
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<tr>
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<td>23.60</td>
<td>18</td>
<td>7.7</td>
<td>4.48</td>
<td>2.02</td>
<td>4.22</td>
<td>10.09</td>
<td>15.17</td>
<td>0.2445</td>
<td>n.</td>
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<tr>
<td>OF16</td>
<td>26.60</td>
<td>21</td>
<td>7.9</td>
<td>4.49</td>
<td>2.03</td>
<td>4.23</td>
<td>10.08</td>
<td>14.06</td>
<td>0.2446</td>
<td>n.</td>
<td>n.</td>
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<tr>
<td>OF17</td>
<td>28.60</td>
<td>23</td>
<td>8.1</td>
<td>4.55</td>
<td>2.04</td>
<td>4.09</td>
<td>9.79</td>
<td>13.89</td>
<td>0.2467</td>
<td>UA(T,A)</td>
<td>6.6±0.4</td>
<td>2.1</td>
</tr>
<tr>
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<td>30.60</td>
<td>25</td>
<td>7.9</td>
<td>4.54</td>
<td>2.01</td>
<td>4.10</td>
<td>9.89</td>
<td>14.65</td>
<td>0.2498</td>
<td>UA(T,A)</td>
<td>5.8±0.1</td>
<td>-0.5</td>
</tr>
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<td>28</td>
<td>7.9</td>
<td>4.45</td>
<td>2.00</td>
<td>4.10</td>
<td>9.70</td>
<td>14.03</td>
<td>0.2460</td>
<td>n.</td>
<td>n.</td>
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<td>30</td>
<td>7.9</td>
<td>4.46</td>
<td>1.99</td>
<td>4.18</td>
<td>10.24</td>
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<td>37</td>
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<td>2.01</td>
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<td>8.2</td>
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<td>4.03</td>
<td>9.56</td>
<td>14.38</td>
<td>0.2518</td>
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<tr>
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<td>13.90</td>
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<td>7.2±0.4</td>
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<td>135</td>
<td>7.2</td>
<td>4.71</td>
<td>2.08</td>
<td>4.23</td>
<td>10.01</td>
<td>14.30</td>
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<td>UA(T,A)</td>
<td>5.7±0.5</td>
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</tr>
<tr>
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<td>178</td>
<td>6.7</td>
<td>4.97</td>
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<td>4.33</td>
<td>10.19</td>
<td>14.41</td>
<td>0.2547</td>
<td>CE(A,F)</td>
<td>6.7</td>
<td>7.8</td>
</tr>
</tbody>
</table>

(1): Sampling date
(2): Sampling time after start.
(3): Analytical precision: He: 0.4 %, Ne, Ar: 1 %, Kr, Xe: 1.5 %.
(4): Conceptual excess air model (see Chapter 3),
n: no statistically acceptable model fit could be achieved.
The situation is completely different if the dissolved noble gas concentrations in the filter outflow are considered (Fig. 6.3b). Three phases can be distinguished. The first phase is characterized by a fast increase in all dissolved noble gas concentrations. This concentration rise is most pronounced in the case of the light noble gases He and Ne, He increasing by more than 20 % and Ne by more than 15 % in concentration. The initial concentration rise is followed by a period in which the concentrations of the dissolved light noble gases stay nearly constant whereas the heavy noble gas concentrations tend to decrease slowly. After day 11, the concentrations of the light noble gas decrease drastically. During day 12, they reach the inflow concentration level.

Table 6.3: Measured noble gas concentrations in the inflow to the slow filter.

| Sample | SD | ST | T | He | Ne | Ar | Kr | Xe | ^{4}He/^{3}He | Excess Air | T | ΔNe |
|--------|----|----|---|----|----|----|----|----|              | Model        |   |     |
|        | (1) | (2) | (3) | (4) | (5) | (6) | (7) | (8) | (9) | (10) | (11) | (12) |
| IF1    | 5.6.00 | 0 | 7.7 | 4.93 | 2.17 | 4.13 | 9.81 | 14.33 | 0.2514 | UA(T,A) | 6.5 ± 0.6 | 8.5 |
| IF2    | 22.6.00 | 17 | 7.6 | 4.96 | 2.18 | 4.15 | 9.87 | 14.18 | 0.2527 | UA(T,A) | 6.5 ± 0.5 | 8.6 |
| IF3    | 28.6.00 | 23 | 7.7 | 4.92 | 2.14 | 4.12 | 9.71 | 13.90 | 0.2540 | UA(T,A) | 6.9 ± 0.4 | 7.3 |
| IF4    | 3.7.00 | 28 | 7.9 | 4.94 | 2.17 | 4.17 | 9.81 | 14.08 | 0.2519 | UA(T,A) | 6.5 ± 0.4 | 8.1 |
| IF5    | 12.7.00 | 37 | 7.7 | 4.91 | 2.15 | 4.19 | 9.97 | 14.22 | 0.2522 | n.       | –         | –         |
| IF6    | 26.7.00 | 51 | 8.2 | 5.07 | 2.20 | 4.20 | 10.01 | 14.49 | 0.2545 | UA(T,A) | 6.2 ± 0.2 | 8.6 |
| IF7    | 9.8.00 | 65 | 8.4 | 4.68 | 2.07 | –    | –    | –    | 0.2502 | UA(A)    | 8.4        | 5.2 |
| IF8    | 30.8.00 | 86 | 7.9 | 4.91 | 2.14 | 4.24 | 10.11 | 14.54 | 0.2533 | UA(T,A) | 5.6 ± 0.4 | 5.7 |
| IF9    | 13.9.00 | 100 | 8.3 | 4.83 | 2.11 | 4.20 | 10.04 | 14.39 | 0.5119 | UA(T,A) | 5.8 ± 0.3 | 4.5 |
| IF10   | 18.10.00 | 135 | 7.2 | 4.87 | 2.13 | 4.21 | 10.20 | 14.50 | 0.2526 | UA(T,A) | 5.6 ± 0.4 | 5.2 |
| IF11   | 29.11.00 | 178 | 6.7 | 4.99 | 2.17 | 4.29 | 10.28 | 14.96 | 0.2537 | CE(T,A,F) | 6.5 ± 1.4 | 7.6 |

(1): Sampling date
(2): Sampling time after start.
(3): Analytical precision: He: 0.4 %, Ne: 1 %, Ar: 1 %, Kr: 1.5 %.
(4): Conceptual excess Air model (see Chapter 3),
  n: no statistically acceptable model fit could be achieved.
Figure 6.3: Dissolved relative noble gas concentrations (a) in the filter inflow and (b) in the filter outflow. Note that the concentrations in the inflow are given relative to the first measured concentration, whereas the concentrations in the outflow are expressed relative to the concentrations in the water inflow.
The first samples taken in the filter outflow are slightly undersaturated with regard to the corresponding concentrations in the filter inflow. This may indicate an incomplete displacement of the residual drinking water from the first purification stage by rapidly filtered raw water at this very early phase. While the regular drinking water should be more or less in solubility equilibrium with the atmosphere, the raw water already contains a dissolved gas excess. The drinking water residuals in the filter sand can therefore lead initially to a small decrease in the dissolved gas concentrations in the raw water and thus to an apparent undersaturation with respect to the initial inflow concentrations.

The second stage, starting at day 13, is dominated primarily by a continuous, steady decrease in the concentrations of all noble gases. In the case of the light noble gases, a level is soon reached at which the concentrations are 10 % lower than those in the water inflow. This concentration level corresponds to their atmospheric solubility equilibrium. The decrease in the heavy noble gas concentrations is attenuated, but nevertheless they also fall below their input concentrations (day 51). In the second part of this phase, all noble gas concentration start to rise, and by day 86 the dissolved concentrations in the filter outflow correspond approximately to the input values.

In the third stage, starting at day 86, smaller temporal variations in the dissolved noble gas concentrations are present. The general evolution of the outflow concentrations in this part of the study is very similar to that of the inflow concentrations. Larger fluctuations in the dissolved composition are not observable.

The separation of the measured noble gas data into three groups can also be visualized by plotting the He and the Xe concentrations (Fig. 6.4). Xe reacts most sensitively to temperature, whereas He reflects mainly the effects of excess air. In general, the overall spread in the Xe concentrations is significantly smaller than that in the He concentrations. The supersaturation pattern is evidence for the dissolution of entrapped air bubbles being responsible for the generation of the observed gas excess (Stute and Schlosser, 2000).
If we focus on the He concentrations, the samples from the first stage have enriched He concentrations of between $5.5 \cdot 10^{-8}$ and $6.1 \cdot 10^{-8}$ cm$^3$ STP.g$^{-1}$. The He concentrations of the second stage samples fall between the atmospheric solubility equilibrium value ($4.53$ cm$^3$ STP.g$^{-1}$ at 7 °C) and the typical He concentrations of 4.8 to 4.9 cm$^3$ STP.g$^{-1}$ in the inflow. The samples that cluster around the solubility equilibrium concentrations clearly show the significant decrease in the light noble gases below the inflow concentrations.

The third stage samples group around the measured inflow concentrations.

The observed spread in the Xe concentrations seems to reflect temperature variations in the raw water. Regarding the first three months of the study, the raw water temperatures generally undergo a slight increase in response to higher groundwater tempera-
tures. In the last three months of the study, especially at the beginning of autumn, water temperatures decrease and the concentrations of the heavy noble gases tend to increase in direct response to this.

6.4 Discussion

The dissolved noble gas concentrations in the slow filter were monitored over a period of six months after it had been put into operation again. The main goal of this study was to decide whether the same physical processes that control the gas exchange in the laboratory sand columns also govern gas/water partitioning in porous media on larger scales. To facilitate discussion of the measured results of this study, in the following we will consider and discuss the noble gas data from the three distinct phases of the study separately.

6.4.1 First phase (Day 1 – Day 12)

The concentration profiles of the first phase of gas dissolution dynamics in the sand filter seem very similar to those expected from the laboratory column throughflow experiments in Chapter 5.4.2. For these column experiments, the kinetic bubble dissolution (KBD) model predicted dissolved concentration profiles that are characterized by a fast increase, a plateau-like quasi-steady state phase and – connected with the continuous bubble dissolution process – a final concentration decrease related to the collapse of entrapped air bubbles.

To analyze the measured concentration profiles, the first phase of the slow filter restarting operation is therefore simulated using the KBD model with the parameters of Table 4.1 (hydrostatic overload). The only unknown parameters in the simulation are the initial bubble size distribution of the entrapped air (initial bubble radius and distribution of different-sized bubble classes) and the air-water ratio in the pore space. All
other model parameters are set either by the geometry of the filter or by the operating procedure of the starting process. The unknown parameters were optimized to fit the measured data.

The results of the simulation are very highly consistent. The light noble gases in particular exhibit a very high consistency between the simulation results and the measured data (Fig. 4.6). The measured heavy noble gas concentrations also agree with the theoretical profiles for vertical advective water flow. After an initial increase, the dissolved concentrations of Ar, Kr and Xe decline towards their quasi-steady state level. The higher the solubility of the gas, the greater is the rate of this decrease.

If the dissolved noble gas composition is interpreted using the available bulk excess air models (UA, CE and PR models, Chapter 3), the temporal evolution of the composition obeys the same pattern predicted by the KBD model. Samples taken during the initial concentration rise and the first part of the plateau-like concentration profile show a fractionated excess air composition analogous to the closed-system equilibration (CE) approach. Samples taken later in the first phase tend to have a pure atmospheric excess composition. Nevertheless, the composition of some samples cannot be explained by the available excess air models.

One prominent conclusion can be drawn from the very good agreement existing between the measured light noble gas data that react most sensitively to the presence of excess air, and the simulations of the KBD model. In this first phase of the re-starting, the evolution of the dissolved gas composition in the sand filter experiment is clearly dominated by the presence of entrapped air and its continuous dissolution. Furthermore, the larger spatial dimensions of the system seem not to have an obvious effect on the process of excess air generation.
6.4.2 Second phase (Day 13 – Day 86)

The dissolved noble gas concentrations show a decrease in the first part of the second phase and a subsequent rise in the second part. Especially in the first part (day 13 – day 51), the effectiveness of the concentration decrease is influenced by the different physical properties of the noble gases: the lighter the gas, the more drastic is the initial decrease (Fig. 6.3).

The evolution of the noble gas concentration is not explicable a priori using the ideas of excess air formation available so far. Consequently, the bulk excess air models are mostly not capable of reproducing this sharp decrease correctly (Tab. 6.2). Even for those samples that can be explained conceptually, the noble gas temperatures determined are significantly lower than the measured water temperature, giving further evidence that the dissolved gas patterns are not reproduced correctly.

What is the dominating process for this selective decrease that affects all noble gases but favors the light ones? Since detailed measurements from within the matrix of the filter are missing, and the experiment cannot be easily repeated, any proposed solution has to remain speculative. As a basis for a discussion of this phenomenon, the following aspects have to be re-considered:

1. The first phase is obviously influenced by the dissolution of entrapped air bubbles. By the end of phase 1, most of this entrapped air should have been removed.
2. In general, the concentration profiles of phase 3 in the water inflow and in the outflow samples evolve similarly with time.
3. At the beginning of phase 2, $^{4}\text{He}$ is depleted significantly relative to $^{20}\text{Ne}$ (Tab. 6.2); hence the $^{4}\text{He}/^{20}\text{Ne}$ ratios are significantly lower than those of water in atmospheric solubility equilibrium at 7 °C (0.2506). Most probably, this decrease in the $^{4}\text{He}/^{20}\text{Ne}$ ratios indicates a diffusive change in the dissolved gas composition. Since the diffusivity of $^{4}\text{He}$ in water is approximately twice that of $^{20}\text{Ne}$, diffusive changes in the dissolved gas composition act more efficiently for $^{4}\text{He}$. As a result,
the diffusive alteration of an initially dissolved gas excess leads to a decrease in the $^4\text{He}/^{20}\text{Ne}$ ratio that can even be below the solubility equilibrium value.

To obtain a decrease in the concentrations of the dissolved noble gases, as in phase 2, a different diffusively controlled gas exchange process has to be assumed in addition to that acting between entrapped air and water. Such a second type of diffusive mass transfer may occur:

1. at the boundaries of the system considered, i.e., either across the free water surface or during the sampling procedure; or
2. between the dissolved gas component and a second domain that operates on a longer time scale than gas exchange between water and entrapped air bubbles.

To evaluate the first assumption, we performed a mass balance for He and Ne over the whole study period. If diffusive gas losses at the system boundary were responsible for the decrease in light noble gases, the mass balance allows such gas losses to be detected. The results for the He and Ne mass balances are shown in Table 6.4.

**Table 6.4:** He and Ne mass balance over the studied period in the slow filter.

<table>
<thead>
<tr>
<th></th>
<th>Inflow</th>
<th>Outflow</th>
<th>Difference</th>
</tr>
</thead>
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<tr>
<td>Balance period</td>
<td>05.06.2000 – 29.11.2000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total discharged water volume</td>
<td>791 000 m$^3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total dissolved He</td>
<td>38 770 cm$^3$</td>
<td>38 400 cm$^3$</td>
<td>1.0 %</td>
</tr>
<tr>
<td>Total dissolved Ne</td>
<td>169 500 cm$^3$</td>
<td>171 000 cm$^3$</td>
<td>- 0.9 %</td>
</tr>
</tbody>
</table>

Obviously, the mass balance works out: during the six month period of investigation, the amounts of He and Ne entering the slow filter by the water inflow equal those measured in the outflow. Diffusive gas losses at the boundaries of the filter are therefore most probably not responsible for the observed concentration decrease.
Regarding the second explanation, two theoretical realizations of a diffusively controlled gas exchange between physically different domains in the filter are shown in Figure 6.5.

In the first case, parts of the dissolved gas excess in the water-filled first domain are transferred diffusively into a gas-filled second domain (Fig. 6.5a). The water-filled volume with advective flow represents the largest part of the quartz sand in the filter, whereas the second gas reservoir is significantly smaller. The gas exchange velocity of this additional gas reservoir has to be relatively small in order to ensure the long-term stability of the gas phase. While in the first phase of the study the dissolution of entrapped air bubbles in the filter sand dominates the dissolved gas composition, with the extinction of most of the entrapped air at the end of phase 1, the gas exchange between the dissolved component and the additional gas reservoir becomes increasingly important. As a result, a characteristic decrease in the dissolved noble gases favoring the light noble gases can be expected.

One obstacle to this concept is the influence of hydrostatic and capillary pressure acting on the gas phase. If the gas phase is assumed to consist of atmospheric air, the increased pressure in the filter will enhance dissolution of the gas phase, even if the water in the filter is already supersaturated. The presence of a reservoir free of noble gases may therefore be more suitable to explain the observed pattern (Bosch and Mazor, 1988).

In the second case, the dissolved gas excess in the advective water volume is partly transferred into a stagnant, water-filled second domain that is in atmospheric solubility equilibrium (Fig. 6.5b). The higher the solubility of a gas, the smaller is the concentration gradient between the two regions. Therefore, as the diffusion coefficients of the highly soluble gases in water are small, a selective gas transfer into the stagnant water body may occur which favors the light noble gases.
Since the water volume needed to facilitate the observed reduction of the excess air amount (day 12 – day 86) is approximately half the total discharged water volume of this period, the explanation of concentration decrease in the filter using a stagnant water volume is rather unrealistic.

Figure 6.5: Possible realizations of a diffusively controlled dual-domain gas exchange concept that leads to a preferential decrease in the light noble gases in the larger main domain. Fig. 6.5a considers the second domain to be a gas-filled reservoir, Fig. 6.5b assumes this second domain to be filled with stagnant water in atmospheric solubility equilibrium. $C^*$ denotes the corresponding equilibrium concentration.

Further discussions on dual domain gas exchange in the slow filter have to remain speculative because detailed data from within the filter are not available. Nevertheless, the effectiveness of such a type of gas exchange and its consequences for the dissolved gas composition are well known in hydrogeology. Especially for He, the influence of a secondary porosity on the dissolved transport is well documented (Carter et al., 1959; Eikenberg et al., 1992; Gupta et al., 1994). Although we cannot definitely identify the process that leads to the observed decrease in the dissolved noble gas concentrations, a diffusively controlled gas exchange between water and an additional domain seems to be evident in the measured data. This favors a process that is at least similar to the proposed mechanisms.
6.4.3 Third phase (Day 87 – Day 178)

The last stage of putting the slow filter into operation is characterized by a gentle increase in the dissolved concentrations. The general evolution in the outflow samples follows that of the concentrations in the filter inflow (Fig. 6.3). The absence of any kind of significant gas exchange process that alters the dissolved gas composition in the sand filter is a clear indication that the entrapped air volume in the sand is most likely completely dissolved. Furthermore, any possible enclosed gas reservoir is apparently in steady-state equilibrium with the inflow water composition. As a result, no effective changes in the dissolved gas composition are to be expected, which is in good agreement with the measured data.

6.4.4 Excess air formation and scale dependence

The present study exhibits new and unexpected results concerning the dissolved gas dynamics in a simple throughflow system, especially during the second and third phases of the period of observation. If we focus on the process of excess air formation, the first phase of the filter re-starting confirms and is in good agreement with almost all findings from the laboratory column experiments in Chapter 5. Vertical water movements in natural porous media always lead to the entrapment of air bubbles. Assuming a vertical advective water flow, such entrapped air bubbles have to dissolve completely as the air reservoir is steadily replenished by the continuous water flushing. The entrapped air dissolution results in a dissolved excess component that initially has a fractionated composition favoring the heavier noble gases, analogous to the CE concept. With ongoing dissolution, the excess air component evolves towards unfractionated, pure excess air. This general behavior and the temporal evolution of the dissolved gas composition remain the same in both the small laboratory column experiments and in the larger scale sand filter. Hence the scale-up of spatial dimensions seems not to have any obvious and direct influence on the formation of excess air.
Furthermore, although the filter inflow already contains a dissolved gas excess, the measured outflow concentrations agree with model predictions based on the column experiments. This adds further credence to the developed concept of gas/water partitioning in porous media as the model correctly reproduces measured data independently of specific boundary conditions. Finally, the increase in heterogeneity of the porous medium in the filter in comparison to the column experiments has no observable effect on the dissolution of atmospheric gases during the first phase of excess air formation.

In phase 2 of the study, after the entrapped air has been removed from the filter, a more pronounced influence of the increased heterogeneity on the dissolved gas composition may be more likely, or at least cannot be completely excluded. Thus the presence of a second domain in the filter that can explain the observed decrease of the noble gas concentrations in phase 2 may be a consequence of the structural heterogeneity in the filter material.

6.5 Conclusions

In the present study, the formation of excess air in the quasi-saturated quartz sand of a large slow filter with advective flow regime was investigated over six months. The first phase of the study is characterized by an increase in the dissolved gas concentrations in reaction to the dissolution of entrapped air. The temporal evolution of the dissolved concentrations is in very good agreement with results from laboratory column experiments (Chapter 5) and simulations employing the kinetic bubble dissolution model. This consistency supports on the one hand the validity of the results and the conclusion drawn from the column experiments and indicates the applicability of the proposed concept of excess air formation. On the other hand, the absence of any observable effect of the spatial and temporal scale-up suggests that the scale of the system is un-
likely to have more than a weak influence on the process of excess air formation. Both aspects can be reasonably considered as indicators of the correctness and robustness of the concept of excess air generation as developed here. This concept therefore provides an important step towards obtaining a physically sound description of gas/water partitioning in porous media.
Chapter 7

Noble gas and major element constraints on the water dynamics in an alpine floodplain

Johannes Holocher, Vijay Matta, Werner Aeschbach-Hertig, Urs Beyerle, Markus Hofer, Frank Peeters, and Rolf Kipfer

Abstract

The hydrogeological system of an ecologically sensitive alpine floodplain in the Valle di Blenio, Switzerland, was investigated using hydrochemical and $^3$H-$^3$He dating methods. Water samples from six wells and from different surface locations were analyzed. The analysis of the concentrations of major ions in conjunction with age determination by the $^3$H-$^3$He-method allowed the main hydrological properties of the system to be consistently characterized. Two geochemically distinct water zones can be distinguished: Ca-SO$_4$-dominated water from the main river and Ca-HCO$_3$-dominated floodplain water. The floodplain water component characterizes the whole floodplain including the surficial hillslope drainage system. Within the groundwater samples, two spatially and temporally different types of water can be determined. A younger (age < 1.5 yr), less mineralized water is found in the upper part of the aquifer during the summer season. The underlying aquifer zone contains older and more highly mineralized water. However, the general hydrochemical characterization of both types of groundwater is similar. In winter, the water ages increase with decreasing groundwater levels. Because precipitation is stored temporarily in the snow cover, the contribution of the younger near-surface groundwater decreases, resulting in higher apparent water ages and higher mineralization in the upper zone of the aquifer. Water exchange between the main river and the groundwater system is limited to groundwater exfiltration from the shallow aquifer zone, whereas the hydrochemical separation of the deeper aquifer zone indicates the isolation of the deeper groundwater from the main river.
7.1 Introduction

Riverine floodplains are a key element in the hydrology of catchment systems. Besides offering a widespread variety of habitats for flora and fauna of exceptional ecological importance (Ward et al., 1999), floodplains can influence the chemical river water quality (Hemond, 1980; Tockner et al., 1999) and the stream discharge regime (Bradley, 1996). Floodplains are becoming increasingly subject to anthropogenic disturbance due, for instance, to stream discharge regulations or the extraction of groundwater for use as drinking water. To preserve their ecological and economical value, it is necessary to take measures to ensure that floodplains are utilized wisely. As a prerequisite, the flow and transport mechanisms in such systems must be known. Of special interest is the quantification of the hydrological connection between stream and floodplain aquifer and the different proportions of groundwater and surface water existing within the floodplain (Alden and Munster, 1997). This can be crucial – even on a conceptual level – since the hydrology of such a system is often complex and reliable information on the water flow dynamics is seldom available.

The use of environmental tracers can help to provide this lacking knowledge, since these tracers are an important tool for the identification and quantification of different water components in hydrogeology. They allow groundwater to be distinguished from surface water (e.g., Plummer et al., 2000), groundwater contamination to be characterized (e.g., Dunkle Saphiro et al., 1999), and geochemical transformation processes to be identified (e.g., Mengis et al., 1999).

In this paper, tritium ($^{3}$H) and dissolved noble gases were used as environmental tracers in combination with hydrochemical data to gain more detailed insights into the mechanisms controlling the hydrology of a Swiss alpine floodplain in the Valle di Blenio. The combined isotopic-hydrochemical approach employed was particularly intended as an aid in determining possible interactions between stream water and groundwater in this ecologically important floodplain.
7.2 Study area

The Valle di Blenio is located in the southern Alps in the Canton of Ticino, Switzerland (Figure 7.1). Starting in Biasca (303 m a.s.l.), the valley extends over 20 km in a north-south direction up to Olivone (890 m a.s.l.). The River Brenno has two main source areas which join near Olivone: the Valle Santa Maria with the Passo del Lucomagno (1915 m a.s.l.) and the Valle Camadra. There are three major floodplains along the Brenno. This study focuses on the middle floodplain on the western side of the Brenno between Grumo and Aquarossa. The vegetation of the floodplains in the Valle di Blenio consists mainly of meadows and partly wooded areas. These alpine floodplains with their typical flora and fauna are of such ecological importance that they are protected under Swiss federal legislation.

The River Brenno (average discharge: 4.75 m³/s) is strongly influenced by hydropower production within its catchment area. Three reservoirs with a combined capacity of up to 3.1×10⁵ m³ and three hydropower plants (Biasca, Olivone, Luzzone) operate in the Brenno catchment area.

Geologically, the Blenio region is part of the lower penninic nappes in the Ticino sub-Dome (Pastorelli et al., 1999). It consists mainly of pre-Triassic crystalline series of gneiss and schists and carbonate-rich Mesozoic sediment layers. The crystalline and sediment layers were subjected to strong tectonic deformations associated with the updoming process. As a result, both types of layers were back-folded with a strong fracturing of the crystalline series (Preiswerk et al., 1934; Ammann, 1973). The study area consists of gneiss and paragneiss of the Lucomagno-Leventina nappe and a dolomitic sediment cover layer, mainly in the northern part between Grumo and the Uregn tributary.
7.3 Sample collection and analysis

In this study, sampling was confined to the middle floodplain. Sampling was carried out in six wells (VB1 to VB6) and two groups of piezometers (PU and PQ), and in the Brenno and Uregn rivers (Figure 7.1). The diameters of the wells varied from 10 cm (VB2) to 14 cm (VB3) and their depths from 9.1 m (VB1) to 18.8 m (VB2). Each of the wells had a screened casing over its entire saturated length. The piezometers used were steel tubes of 4 cm diameter that extended from the surface down to depths of either 1.5 m or 2 m. The lowermost 70 cm of each piezometer was perforated. The groundwater samples from the wells and piezometers were taken by submersible
Sample collection and analysis

pumps from the depth indicated in Table 7.1. To test whether the groundwater accessible by the wells represents one homogeneous hydrochemical zone, profiles of temperature and electrical conductivity were measured in the wells prior to sampling. If these profiles showed significant changes with depth, two samples from the upper and the lower part of the well screening were taken, employing a dual pumping technique (Rapp et al., 1998).

To record the annual evolution of the groundwater system, five sampling campaigns were carried out between February 1998 and February 1999. In February 1999, an additional sample was taken from a spring on a small island within the active river bed of the Brenno (VBup). The upwelling water in this spring discharges at an elevation 3–5 m higher than the riverine water level. The temperature and electrical conductivity indicated that this spring releases groundwater not affected by river water.

Water samples of 1 liter were taken in PET bottles for chemical analysis and 45 ml were sealed off in copper tubes with pinch-off clamps (Kipfer, 1991; Beyerle et al., 2000) to measure dissolved noble gases.

For all five sampling dates, analyses of major ions were conducted. Concentrations of noble gases ($^3$He, $^4$He, Ne, Ar, Kr, Xe) were measured in the winter, spring and summer samples of 1998, whereas the autumn samples of 1998 and the winter samples of 1999 were analyzed only for He and Ne. Tritium ($^3$H) was measured in the winter, spring and autumn samples of 1998.

The mass spectrometric measurements of the noble gases were performed according to the procedures described by Beyerle et al. (2000). The tritium concentrations of the samples were measured by the $^3$He ingrowth technique (Clarke et al., 1976; Beyerle et al., 2000).
Table 7.1: Hydrochemical and Helium–Neon data. Wells, middle floodplain.

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(2): Given in meters below ground surface.
(3): Average charge balance error: 5%.
(4): Analytical precision: He: 0.4%; Ne: 1%.
7.4 Groundwater dating

7.4.1 $^3$H-$^3$He age calculation

For the determination of water ages younger than 50 years, the radioactive hydrogen isotope tritium ($^3$H) with a half-life of 12.32 years (Lucas and Unterweger, 2000) is widely used in hydrology. Large amounts of tritium were introduced into the atmosphere by atmospheric nuclear weapons tests mainly in the 1960s. With the incorporation of this bomb tritium into the hydrosphere, a time marker for water age determination was available. Additional information about the time elapsed since a water parcel was isolated from gas exchange with the atmosphere can be obtained if tritium and its decay product $^3$He are considered together (Tolstikhin and Kamenskiy, 1969). The $^3$H-$^3$He age defines the time $\tau$ since the gas exchange of a water parcel has stopped, which is the time since the water entered the saturated zone, and is given by (e.g., Schlosser et al., 1989):

$$\tau = \frac{1}{\lambda} \ln \left( 1 + \frac{[^3\text{He}_{\text{eq}}]}{[^3\text{H}]} \right)$$

(7.1)

$\lambda = 0.0563 \text{ yr}^{-1}$ is the decay constant of $^3$H, $[^3\text{H}]$ is the measured tritium concentration and $[^3\text{He}_{\text{eq}}]$ is the tritiogenic $^3$He which is produced in the sample. The conversion of concentration units needed to evaluate Equation 7.1 is given by $1 \text{ cm}^3 \text{ STP/g water} \approx 4.019 \times 10^{14} \text{ TU}$ for fresh water.

To calculate the $^3$H-$^3$He age, it is essential to separate the tritiogenic $^3$He ($[^3\text{He}_{\text{eq}}]$) from the total measured $^3$He ($[^3\text{He}_{\text{tot}}]$). $[^3\text{He}_{\text{tot}}]$ can be resolved into components as follows (Schlosser et al., 1989; Aeschbach-Hertig et al., 1998):

$$[^3\text{He}_{\text{tot}}] =[^3\text{He}_{\text{eq}}] +[^3\text{He}_{\text{exc}}] +[^3\text{He}_{\text{ter}}] +[^3\text{He}_{\text{ni}}]$$

(7.2)
Table 7.2: Hydrochemical data: Surface water and piezometers, middle floodplain

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<td>0.54</td>
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<tr>
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<td>198</td>
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<td>8.9</td>
<td>1.67</td>
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<td>0.31</td>
<td>1.95</td>
</tr>
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<td>207</td>
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<td>0.40</td>
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<td>0.111</td>
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<td>0.114</td>
<td>5.76</td>
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<td>313</td>
<td>7.40</td>
<td>—</td>
<td>2.58</td>
<td>1.14</td>
<td>0.099</td>
<td>0.60</td>
</tr>
<tr>
<td>PU 219</td>
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<td>0.80</td>
<td>1</td>
<td>331</td>
<td>7.50</td>
<td>—</td>
<td>2.68</td>
<td>1.28</td>
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<td>0.67</td>
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<td>PU 214</td>
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<td>0.85</td>
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<td>7.50</td>
<td>—</td>
<td>2.56</td>
<td>1.24</td>
<td>0.098</td>
<td>0.71</td>
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<td>5</td>
<td>2</td>
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<td>1.8</td>
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<td>7.70</td>
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<td>1.00</td>
<td>0.092</td>
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<tr>
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</tr>
<tr>
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<tr>
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<td>7.70</td>
<td>—</td>
<td>4.34</td>
<td>1.66</td>
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<td>1</td>
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<td>4.34</td>
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<td>1</td>
<td>489</td>
<td>7.70</td>
<td>—</td>
<td>4.24</td>
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<td>0.75</td>
<td>1</td>
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<td>8.00</td>
<td>—</td>
<td>5.96</td>
<td>2.02</td>
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<tr>
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<td>1.5</td>
<td>0.80</td>
<td>1</td>
<td>630</td>
<td>7.90</td>
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<td>6.10</td>
<td>2.06</td>
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</tr>
<tr>
<td>PQ 214</td>
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<td>1.5</td>
<td>0.80</td>
<td>1</td>
<td>631</td>
<td>7.90</td>
<td>—</td>
<td>6.12</td>
<td>2.06</td>
<td>0.123</td>
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<tr>
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<td>0.87</td>
<td>1</td>
<td>627</td>
<td>7.90</td>
<td>—</td>
<td>5.90</td>
<td>2.08</td>
<td>0.122</td>
<td>5.22</td>
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</tbody>
</table>


(2): Given in meters below ground surface.

(3): Average charge balance error: 5%.
$^3\text{He}_{\text{eq}}$ is the concentration of $^3\text{He}$ in water in equilibrium with air, $^3\text{He}_{\text{exc}}$ is the excess air component generated by the dissolution of small entrapped air bubbles in the upper part of the saturated zone (Heaton and Vogel, 1981), $^3\text{He}_{\text{ter}}$ is the terrigenic component derived from the earth’s crust or mantle and $^3\text{He}_{\text{tri}}$ is the tritiogenic component. In the study area, the terrigenic $^3\text{He}$ is most likely of crustal origin and therefore henceforth described as radiogenic $^3\text{He}$ ($^3\text{He}_{\text{rad}}$). The equilibrium concentration is determined by temperature, salinity and the atmospheric pressure (altitude) prevailing during groundwater recharge. Measured Ne concentrations are commonly used to determine the excess air component, since the Ne in meteoric water is of atmospheric origin only, and hence the Ne balance consists of the equilibrium and the excess air components only. The tritiogenic $^3\text{He}$ can then be calculated as follows (Schlosser et al., 1989):

$$
^3\text{He}_{\text{tri}} = 4^\text{He}_{\text{tot}} \cdot (R_{\text{tot}} - R_{\text{rad}}) - 4^\text{He}_{\text{eq}} \cdot (R_{\text{eq}} - R_{\text{rad}}) - L_{\text{exc}} \cdot (N_{\text{tot}} - N_{\text{eq}}) \cdot (R_{\text{exc}} - R_{\text{rad}})
$$

(7.3)

where R is the $^3\text{He}/^4\text{He}$ ratio of the respective component and $L_{\text{exc}}$ is the He/Ne ratio of the excess air. To calculate the $^3\text{H}-^3\text{He}$ water age, two quantities have to be established: the He/Ne ratio of excess air ($L_{\text{exc}}$) and the $^3\text{He}/^4\text{He}$ ratio of the radiogenic component ($R_{\text{rad}}$).

Information about $L_{\text{exc}}$ can be obtained from the analyses of the other atmospheric noble gases Ar, Kr, and Xe and the comparison of the noble gas data with the predictions of different excess air models (Aeschbach-Hertig et al., 2000). Information about $R_{\text{rad}}$ may be derived from the dependence of the measured $^3\text{He}/^4\text{He}$ ratios on the He concentration, and in particular from those samples with the highest contributions of radiogenic He (Aeschbach-Hertig et al., 1998). In the following, we will discuss in detail how $L_{\text{exc}}$ and $R_{\text{rad}}$ were derived in this study, because their choice significantly influences the $^3\text{H}-^3\text{He}$ water ages and hence the overall interpretation of the groundwater dynamics in the floodplain.
7.4.2 Determination of the He/Ne ratio of excess air

Atmospheric gases in groundwaters are usually found to be oversaturated with respect to equilibrium conditions (Heaton and Vogel, 1981; Andrews, 1992; Wilson and McNeill, 1997). This “excess air” phenomenon has to be taken carefully into account when calculating recharge temperatures from dissolved noble gas concentrations in groundwater (Stute and Schlosser, 1993; Aeschbach-Hertig et al., 1999). For this calculation the contributions of excess air and solubility equilibrium to the total measured noble gas concentrations have to be resolved. This is done by conceptualizing the excess air component either as (1) pure atmospheric air, (2) air fractionated by partial degassing of an initial excess across the groundwater table (Stute et al., 1995) or (3) air fractionated by equilibration of a finite entrapped air volume with a finite water volume in the quasi-saturated zone (Aeschbach-Hertig et al., 2000). Unfractionated excess air has the atmospheric He/Ne ratio 0.288. If the excess air is fractionated by diffusive degassing, $L_{exc}$ can adopt any value between zero and 0.288. If fractionation is the result of closed-system equilibration with entrapped air, $L_{exc}$ is constrained to range between the He/Ne ratio of air and that of air-saturated water (0.23 to 0.25, depending on temperature).

We applied the inverse technique of Aeschbach-Hertig et al. (1999) for the interpretation of noble gas data to those samples from the Valle di Blenio for which all noble gases had been analyzed, in order to judge which of the proposed excess air models correctly describes the data. The results permitted us to determine the appropriate values of $L_{exc}$ (Table 7.3).

During winter the excess air composition of all samples can be explained by unfractionated excess air ($L_{exc} = 0.288$). In spring and summer, the excess air component was generated by finite air/water volume equilibration (Aeschbach-Hertig et al., 2000) which results in a significantly lower $L_{exc}$. The mean value for $L_{exc}$ of 0.244 that characterizes the spring and summer situation was also assigned to the autumn samples for which no complete noble gas data are available.
Table 7.3: Apparent water ages and calculated noble gas temperatures, middle floodplain.

<table>
<thead>
<tr>
<th>Sample</th>
<th>SD</th>
<th>Depth (m)</th>
<th>$^3$H (TU)</th>
<th>$^3$He (TU)</th>
<th>Age (yr)</th>
<th>NGT (°C)</th>
<th>$\Delta$Ne (%)</th>
<th>Model</th>
<th>$L_{exc}$</th>
</tr>
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<tbody>
<tr>
<td>VB 1</td>
<td>1</td>
<td>8.5</td>
<td>12.66 ± 0.55</td>
<td>6.41 ± 0.92</td>
<td>7.3 ± 0.9</td>
<td>8.4 ± 0.3</td>
<td>10.0</td>
<td>UA</td>
<td>0.288</td>
</tr>
<tr>
<td>VB 3</td>
<td>1</td>
<td>9</td>
<td>13.68 ± 0.61</td>
<td>3.53 ± 0.82</td>
<td>4.1 ± 0.9</td>
<td>5.8 ± 0.3</td>
<td>6.5</td>
<td>UA</td>
<td>0.288</td>
</tr>
<tr>
<td>VB 4</td>
<td>1</td>
<td>9</td>
<td>14.09 ± 0.61</td>
<td>6.04 ± 0.59</td>
<td>6.4 ± 0.6</td>
<td>7.5 ± 0.3</td>
<td>12.2</td>
<td>UA</td>
<td>0.288</td>
</tr>
<tr>
<td>VB 5</td>
<td>1</td>
<td>13</td>
<td>15.19 ± 0.57</td>
<td>7.70 ± 0.68</td>
<td>7.3 ± 0.6</td>
<td>8.7 ± 0.3</td>
<td>8.5</td>
<td>UA</td>
<td>0.288</td>
</tr>
<tr>
<td>VB 6</td>
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<td>9</td>
<td>14.73 ± 0.60</td>
<td>5.11 ± 1.07</td>
<td>5.3 ± 1.0</td>
<td>8.3 ± 0.3</td>
<td>7.0</td>
<td>UA</td>
<td>0.288</td>
</tr>
<tr>
<td>VB 1</td>
<td>2</td>
<td>8.5</td>
<td>10.61 ± 0.15</td>
<td>2.73 ± 0.47</td>
<td>4.1 ± 0.6</td>
<td>9.5 ± 2.1</td>
<td>22.3</td>
<td>CE</td>
<td>0.236</td>
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<tr>
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<td>17</td>
<td>11.02 ± 0.15</td>
<td>1.31 ± 0.25</td>
<td>2.0 ± 0.4</td>
<td>11.0 ± 0.8</td>
<td>19.2</td>
<td>CE</td>
<td>0.234</td>
</tr>
<tr>
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<td>4.5</td>
<td>11.99 ± 0.16</td>
<td>4.48 ± 0.86</td>
<td>5.7 ± 0.9</td>
<td>9.3 ± 0.5</td>
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<td>12.04 ± 0.15</td>
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<td>8.2 ± 1.4</td>
<td>—</td>
<td>—</td>
<td>CE</td>
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</tr>
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<td>13</td>
<td>9.60 ± 0.15</td>
<td>0.69 ± 0.24</td>
<td>1.2 ± 0.4</td>
<td>—</td>
<td>—</td>
<td>CE</td>
<td>0.244</td>
</tr>
<tr>
<td>VB 1</td>
<td>3</td>
<td>4</td>
<td>10.36 ± 2.44 (7)</td>
<td>0.32 ± 0.42</td>
<td>0.5 ± 0.7</td>
<td>9.6 ± 1.0</td>
<td>10.3</td>
<td>CE</td>
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<td>0.07 ± 0.39</td>
<td>0.1 ± 0.7</td>
<td>9.7 ± 0.8</td>
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</tr>
<tr>
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<td>10.36 ± 2.44 (7)</td>
<td>0.56 ± 0.40</td>
<td>0.9 ± 0.7</td>
<td>11.1 ± 2.0</td>
<td>23.1</td>
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<td>9.4 ± 0.6</td>
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<td>39.84 ± 20.55</td>
<td>24.3 ± 6.9</td>
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<tr>
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<td>10.10 ± 0.18</td>
<td>6.04 ± 1.03</td>
<td>8.4 ± 1.1</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.244</td>
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<td>4</td>
<td>1</td>
<td>11.72 ± 0.19</td>
<td>0.82 ± 0.41</td>
<td>1.2 ± 0.6</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.244</td>
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</tbody>
</table>

(2): Given in meters below ground surface.
(3): NGT: Noble gas temperature derived from the dissolved noble gases.
(4): $\Delta$Ne: Ne supersaturation due to excess air, $\Delta$Ne = ($N_{tot}$ - $N_{eq}$)/$N_{eq}$.
(6): $L_{exc}$: He/Ne ratio of the excess air component as predicted by the chosen excess air model. For the autumn samples, the mean of the He/Ne ratios from spring and summer was applied.
(7): For these samples no tritium concentrations were measured. A mean tritium concentration for the summer season (sampling dates May, July, October) of 10.36 ± 2.44 TU was assigned.
This assumption was motivated by the hydrochemical data, which indicate that the autumn samples are hydrochemically similar to the summer samples. As the groundwater upwelling at VBup was sampled in February 1999, its excess air component is described by the atmospheric He/Ne ratio (0.288) which reflects the winter situation.

The use of the best estimate of $L_{\text{exc}}$ yields more reasonable results for the calculated tritiogenic and radiogenic He components than the usual choice of the atmospheric $L_{\text{exc}}$, and hence increases the accuracy of the calculated $^3\text{H}-^3\text{He}$ ages. For example, atmospheric $L_{\text{exc}}$ yields negative values for $^3\text{He}_{\text{tri}}$ and therefore negative $^3\text{H}-^3\text{He}$ ages for VB1 and VB2 in summer, whereas the use of the correct fractionated $L_{\text{exc}}$ for these samples results in small but positive ages that are realistic for the summer situation.

For the samples for which all 5 noble gases were analyzed, noble gas temperatures were calculated by applying the respective excess air model (Table 7.3). The calculated average recharge temperature of $9.4 \, ^\circ\text{C} \pm 1.8 \, ^\circ\text{C}$ for the middle floodplain, assuming a mean elevation of 580 m a.s.l., agrees reasonably well with the mean annual air temperature of $10.4 \, ^\circ\text{C}$ determined for the same elevation on the basis of the 10-yr data set 1989-99 measured at the Comprovasco meteorological station (Figure 7.1).

### 7.4.3 Determination of the radiogenic $^3\text{He}/^4\text{He}$ ratio in groundwater

To determine the isotopic composition of the radiogenic He component, following Stute et al. (1992) and Aeschbach-Hertig et al. (1998) we plotted $^3\text{He}/^4\text{He}$, corrected for excess air, against the reciprocal of the $^4\text{He}$ concentration, corrected for excess air and normalized to the solubility equilibrium concentration $^4\text{He}_{\text{eq}}$ (Figure 7.2). All samples lie close to the mixing line between air-saturated water (ASW) and the sample with the lowest $^3\text{He}/^4\text{He}$ ratio, VBup. The samples are shifted above this mixing line and hence contain an additional $^3\text{He}$ component that is tritiogenic. Even sample VBup is tritium-active (13.8 TU) and most probably also contains tritiogenic $^3\text{He}$. 
Therefore the mixing line does not define \( R_{rad} \) itself, but only an upper limit to \( R_{rad} \) (9.85 \( \times \) \( 10^{-8} \) from the intercept of the line).

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**Figure 7.2:** \(^3\)He/\(^4\)He ratios of groundwater samples, corrected for excess air, versus the reciprocal of the \(^3\)He concentrations, corrected for excess air and normalized to the solubility equilibrium \(^4\)He\(_{eq}\). Since all samples contain tritiogenic \(^3\)He, they have significantly higher \(^3\)He/\(^4\)He ratios than would be expected from binary mixing between air-saturated water ASW and the radiogenic \(^4\)He-dominated upwelling groundwater at VBup.

In order better to constrain \( R_{rad} \), one can assume that the amount of \(^4\)He\(_{rad} \) increases linearly with groundwater residence time owing to continuous \(^4\)He\(_{rad} \) accumulation (Heaton, 1984; Beyerle et al., 1999). Generally, the amounts of \(^4\)He\(_{rad} \) in the samples are relatively large (Table 7.1). This probably reflects the high \(^4\)He\(_{rad} \) production rate in pre-Mesozoic gneissic rock in the Blenio area. Furthermore this may indicate the existence of a \(^4\)He\(_{rad} \) flux into the aquifer that need not necessarily be associated with a groundwater flow. Considering the small spatial dimension of the study area, the \(^4\)He\(_{rad} \) sources are not expected to vary strongly, hence all samples can be used to determine
the $^{4}$He$_{\text{rad}}$ accumulation rate. For the measured samples, Figure 7.3 shows the relationship of $^3$H-$^3$He ages to $^4$He$_{\text{rad}}$ concentrations for different values of $R_{\text{rad}}$. The typical radiogenic value of $R_{\text{rad}}$ from crustal U/Th-decay is $2 \times 10^{-8}$ (Mamyrin and Tolstikhin, 1984), whereas $R_{\text{rad}} = 9.85 \times 10^{-8}$ is defined by Figure 7.2. Those samples which contain only small amounts of $^4$He$_{\text{rad}}$ show little variation in the $^3$H-$^3$He ages calculated, and as a result the choice of $R_{\text{rad}}$ has only a slight influence on the age calculation. The opposite is true for the samples that are highly enriched in radiogenic $^4$He (VB3 (9m, July 1999) and VBup), in which the calculated ages react very sensitively to the choice of $R_{\text{rad}}$.

The relationship between $^4$He$_{\text{rad}}$ and residence time is non-linear, independently of the chosen value for $R_{\text{rad}}$ (Figure 7.3).

![Figure 7.3](image)

Figure 7.3: $^3$H-$^3$He ages calculated for different values of the radiogenic $^3$He/$^4$He ratio ($R_{\text{rad}}$) versus the radiogenic $^4$He component. As the $^4$He$_{\text{rad}}$ concentration is expected to increase with increasing water age, the upper limit for $R_{\text{rad}}$ can be set to $7.9 \times 10^{-8}$. Larger values for $R_{\text{rad}}$ result in ages for VBup that are unrealistically small compared to the high $^4$He$_{\text{rad}}$ enrichment in this sample.
Nevertheless, the water ages must increase with increasing amounts of $^4$He$_{rad}$ since the sources of $^4$He$_{rad}$ are the same in all parts of the system. $R_{rad} = 7.9 \cdot 10^{-8}$ is therefore the upper limit for a realistic value for $R_{rad}$ because only $R_{rad} \leq 7.9 \cdot 10^{-8}$ yields for VBup a $^3$H-$^3$He age that is the oldest of all samples. For larger values of $R_{rad}$, the $^3$H-$^3$He age decreases with increasing $^4$He$_{rad}$ concentrations, i.e., the calculated age for VBup becomes smaller than that for VB3 (9m, July 1998), although VB3 contains less $^4$He$_{rad}$ than VBup (Figure 7.3).

The most realistic value for $R_{rad}$ has to lie between the upper limit of $7.9 \cdot 10^{-8}$ and the radiogenic value of $2 \cdot 10^{-8}$, but it cannot be constrained further based on the noble gas data alone.

Here, the hydrochemistry data can assist in determining $R_{rad}$. In aquifers dominated by carbonate dissolution, the Mg$^{2+}$ concentrations may trace the increasing maturity of groundwater and hence the residence time (Herczeg and Edmunds, 2000).

![Figure 7.4](image)

**Figure 7.4:** Determination of different Mg$^{2+}$ accumulation rates for the limiting values of $R_{rad}$ based on all groundwater samples with robust $^3$H-$^3$He ages that are insensitive to the choice of $R_{rad}$. Samples for which the calculated residence time is strongly linked to the chosen value of $R_{rad}$ (VBup; VB3, 9m July 1998) are excluded.
The release of Mg$^{2+}$ by calcite dissolution results in an increase in Mg$^{2+}$ concentrations with increasing residence time until a geochemical equilibrium is reached. Since calcite dissolution is an important process in the aquifer studied, we used Mg$^{2+}$ as an independent variable for a qualitative age indication which measures the ongoing dolomite dissolution.

A temporal accumulation rate for Mg$^{2+}$ could be defined for the study area (Figure 7.4). The samples with small amounts of $^4$He$_{rad}$ and robust $^3$H-$^3$He ages that are insensitive to the choice of $R_{rad}$ were used to define the Mg$^{2+}$ accumulation rate, whereas the $^4$He$_{rad}$-rich samples VBup and VB3 (9 m, July 1998) were excluded. The $^3$H-$^3$He ages were determined for $R_{rad} = 7.9 \cdot 10^{-8}$ and $R_{rad} = 2.0 \cdot 10^{-8}$, resulting in two distinct accumulation rates. Table 7.4 compares the $^3$H-$^3$He ages depending on the choice of $R_{rad}$ for VBup and VB3 (9 m, July 1998) with their corresponding Mg$^{2+}$ accumulation ages. The agreement between the two independently calculated ages of the two samples depends strongly on the value assigned to $R_{rad}$. In this study, we therefore used an intermediate value of $6.0 \cdot 10^{-8}$ for $R_{rad}$, which minimizes the RMS deviation between the two differently calculated ages. To account for systematic uncertainties in defining $R_{rad}$, we assigned a relatively large error of $\pm 2.0 \cdot 10^{-8}$ to $R_{rad}$.

<table>
<thead>
<tr>
<th>$^3$H-$^3$He age</th>
<th>Mg$^{2+}$ accumulation age</th>
<th>$^3$H-$^3$He age</th>
<th>Mg$^{2+}$ accumulation age</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{rad} = 2.0 \cdot 10^{-8}$</td>
<td>24.2 yr</td>
<td>15.1 yr</td>
<td>34.5 yr</td>
</tr>
<tr>
<td>$R_{rad} = 7.9 \cdot 10^{-8}$</td>
<td>15.5 yr</td>
<td>10.8 yr</td>
<td>16.2 yr</td>
</tr>
<tr>
<td>$R_{rad} = 6.0 \cdot 10^{-8}$</td>
<td>18.5 yr</td>
<td>12.3 yr</td>
<td>24.3 yr</td>
</tr>
</tbody>
</table>
To verify the apparent groundwater ages that were calculated with the adopted value of $R_{rad}$, the initial tritium content of the samples can be compared with the tritium record of regional precipitation (Stute et al., 1997; Aeschbach et al., 1998). The initial tritium content is defined by the sum of the measured tritium concentration and the $^3$He produced by tritium decay ($^3$He$_{tr}$) during groundwater flow. The calculated initial tritium is compared to the tritium record in precipitation from Locarno, which is located about 40 km south of the Valle di Blenio (Figure 7.5).

**Figure 7.5:** Tritium record in the precipitation at Locarno, Ticino, Switzerland and the initial tritium concentrations ($^3$H$_{measured} + ^3$He$_{tritiogenic}$ [TU]) of the ground water samples. The samples are plotted on the time axis according to their $^3$H-$^3$He ages. The initial $^3$H concentrations correlate well with the $^3$H record in the local precipitation. The correspondence adds further evidence that the value of $R_{rad}$ in this study was chosen correctly.
The Locarno record lists measured tritium data until 1998. Generally, the calculated initial tritium values agree well with the atmospheric tritium record; even the oldest sample VBup matches reasonably if we consider its error in age of 7 yr. As shown, the abundance of tritiogenic \(^3\text{He}\) in VBup depends strongly on the value of \(R_{\text{rad}}\) used in the \(^3\text{H}-^3\text{He}\) age calculations (Figure 7.3). Therefore, the agreement between the initial tritium content of VBup and the corresponding tritium concentration in precipitation supports the choice of \(R_{\text{rad}} = 6.0 \times 10^{-8} \pm 2.0 \times 10^{-8}\) to calculate the \(^3\text{H}-^3\text{He}\) ages.

In summary, we have established local values of the radiogenic \(^3\text{He}/^4\text{He}\) ratio \(R_{\text{rad}}\) and the \(\text{He}/\text{Ne}\) ratio of the excess air component \(L_{\text{exc}}\) that are used in this study. Despite the importance of these two parameters for the calculation of the tritiogenic \(^3\text{He}\) component (Equation 7.2) and the corresponding \(^3\text{H}-^3\text{He}\) ages (Plummer et al., 2000), they are often poorly determined. The analysis and comprehensive interpretation of all noble gases and the additional use of a geochemical maturity indicator can significantly improve the quality of the \(^3\text{H}-^3\text{He}\) groundwater age determination, particularly if larger excess air and radiogenic components are present.
7.5 Results and discussion

7.5.1 Groundwater head data

The groundwater levels in the floodplain show a definite seasonal variation. Throughout the winter season they are generally low, showing the influence of temporary storage of precipitation in the snow cover which decreases active groundwater recharge and hence the groundwater levels in the floodplain. With the beginning of snowmelt in spring, the water levels rise. In summer, infiltration of fresh water into the aquifer leads to high groundwater heads that fluctuate only slightly in response to precipitation events. As the fresh water supply is reduced in autumn, the groundwater levels decrease, again attaining their minimal values in winter. The absolute annual changes of the groundwater heads vary between 20 cm (VB3) and 7.30 m (VB2). The water level fluctuations are small in the wells that are close to the active River Brenno bed (VB3, VB4, VB6), whereas the more distant wells (VB2, VB1, VB5) are subject to much stronger changes. Generally, the groundwater levels in all wells lie above the riverine water level of the Brenno throughout the entire year.

7.5.2 Hydrochemistry and water components

The hydrochemistry of the middle floodplain, Valle di Blenio, is dominated by the major ions calcium (Ca\(^{2+}\)), magnesium (Mg\(^{2+}\)), bicarbonate (HCO\(_3^{-}\)) and sulfate (SO\(_4^{2-}\)). Figure 7.6 depicts the composition of the water samples in terms of these major ion components, which comprise 95 % or more of the total dissolved solids. Two different hydrochemical components can be distinguished: water from the River Brenno (Brenno water) and water from the floodplain (floodplain water).
The Brenno water defines the samples from the Brenno itself and from the piezometers in its active riverbed (PQ). The floodplain water represents the six wells (VB1–VB6), the floodplain piezometers PU and samples from the Uregn tributary.

**Figure 7.6:** Hydrochemistry of floodplain water samples (a) and Brenno water samples (b). Since the hydrochemistry in the study area is dominated by Ca\(^{2+}\), Mg\(^{2+}\), HCO\(_3\)\(^-\) and SO\(_4\)\(^{2-}\), the relative composition of the samples in terms of these four ions is displayed. The samples from the Brenno and the piezometers PQ mark a separate hydrochemical component that is dominated by Ca\(^{2+}\) and SO\(_4\)\(^{2-}\). Floodplain well samples taken in winter differ from those taken in other seasons with respect to their significantly higher SO\(_4\)\(^{2-}\) concentrations.

The Brenno water is characterized by high sulfate and low bicarbonate concentrations; in contrast, the floodplain water has high HCO\(_3\)\(^-\) and low SO\(_4\)\(^{2-}\) concentrations. The differences in the cationic composition are less pronounced. The Brenno water contains a somewhat greater proportion of calcium and a smaller proportion of magnesium than...
Results and discussion

the floodplain water, although calcium is the dominant cation in both water components (Tables 7.1, 7.2). The Brenno water is classified as Ca-SO₄ water and the floodplain water as Ca-HCO₃ water.

This separation documents the influence of the geological setting on the hydrochemistry of the system. The floodplain with the River Uregn, together with the groundwater system (wells and piezometers PU) define one hydrochemical unit that is governed by the carbonates and metamorphic rocks of the hillslope. In contrast, the Brenno water that controls the hydrochemistry of the waters in the active river bed gains its characteristically high SO₄²⁻ concentration by upstream dissolution of anhydrite in the upper part of the Val di Lucomagno and sulfate-rich inflows from the neighboring anhydrite-rich Val Piora.

The chemistry of the Brenno as well as that of the floodplain water in the major tributary Uregn and in the piezometers PU remains largely constant throughout the year (Figure 7.6). The composition of the floodplain water in the wells, however, shows a seasonal variation. The well samples taken in winter are generally more mineralized than during the rest of the year, with the largest increase in SO₄²⁻ concentrations (Table 7.1). Because in winter the fresh water supply to the aquifer is reduced, the proportion of older, higher mineralized water in the wells increases. However, short warmer periods can lead to temporary dilution effects by snowmelt water. This explains the spread that is present in the hydrochemistry of the winter samples, ranging between the highly mineralized composition of the groundwater sample from VBup and the rather fresh composition of the samples VB1, VB2 and VB3 taken in February 1999 (Table 7.1). In contrast, during the summer season all wells show the influence of recently infiltrated fresh water, which manifests itself in less mineralization and higher groundwater levels.
Figure 7.7: Hydrochemistry of groundwater samples (a) and surface and near-surface water samples (b) expressed as $\frac{K^+}{Mg^{2+}}$ versus $\frac{SO_4^{2-}}{Mg^{2+}}$ molar ratios. Within the surface water samples the separation in floodplain water (Uregn and piezometers PU) and Brenno water (Brenno and piezometers PQ) is obvious. Within the groundwater samples two different hydrochemical facies exist. The winter samples represent a more evolved groundwater type whereas the summer samples contain recently infiltrated fresh water.

Apart from the seasonal variation, a spatial variation can also be found in the floodplain groundwater samples. Looking at VB3 in May and July, the groundwater in the well is divided vertically into two different zones: an upper layer with the low ion concentrations typical of the summer situation, and a deeper layer with higher ion concentrations and a hydrochemical composition similar to that of the highest mineralized groundwater sample VBup. The Ca-HCO$_3$-floodplain water in the aquifer can therefore be subdivided into two different chemical facies of the same general type (Figure 7.7a): near-surface water (summer component) that is less mineralized (Table 7.1), and more highly mineralized, evolved groundwater (winter component) which is present also in summer in the deeper layer of VB3.
The results of Pastorelli et al. (1999), who analyzed different cold and warm springs in the Valle di Blenio, corroborate the conceptual interpretation in terms of two geochemical facies in the floodplain aquifer. The springs from the western hillslopes between Acquarossa and Grumo are all of Ca-HCO₃ to Ca-HCO₃-SO₄ composition, and their in-situ temperatures correspond to the mean annual air temperature. Pastorelli et al. (1999) interpret the Ca-HCO₃ springs as the result of rock/water interaction of meteoric waters with gneisses and dolomites. In their view, the Ca-HCO₃-SO₄ springs represent a more evolved variety of this fresh Ca-HCO₃ water type. This interpretation is in accordance with our distinction of two geochemical facies in the floodplain with a fresh summer water type of Ca-HCO₃ composition and a more evolved winter water type that tends toward a Ca-HCO₃-SO₄ composition. Pastorelli et al. (1999) also analysed one spring from the Passo di Lucomagno which shows clearly the Ca-SO₄ composition of water from the upper Lucomagno region which is described as Brenno water in our study.

7.5.3 $^3$H-$^3$He dating and noble gas data

The groundwater ages support the conceptual picture of two geochemically distinct groundwater zones, as implied by the hydrochemical data. In winter, all water ages are relatively high (4–7 yr). These high ages correspond to the geochemically more evolved winter groundwater component.

The sample of the upwelling groundwater at VBup is $^3$H-active and highly enriched in radiogenic $^4$He ($^4$He$_{rad} = 98\%$ of $^4$He$_{tot}$). The simultaneous occurrence of $^3$H and $^4$He$_{rad}$ may be interpreted as a mixture of old, tritium-free water and groundwater of the regular winter type. Although an exact separation of these components is not possible based on the data available, there are two strong arguments for believing that only a minor proportion of the VBup water can be tritium-free. Firstly, the calculated initial tritium content of the VBup sample agrees well with the tritium content of the precipitation at the time of infiltration (Figure 7.5). Secondly, tritium-free groundwaters found
in the Valle di Blenio are deep, geothermal waters with total dissolved solids (TDS) exceeding 2400 mg/l (Mazor and Vuataz, 1990). The temperature of VBup and its lower mineral content (TDS = 1230 mg/l) therefore preclude a major contribution of such tritium-free geothermal waters to the upwelling groundwater at VBup.

In spring, the apparent ages in the wells decrease to 1–4 yr, reflecting increasing dilution with recently infiltrated snowmelt water. An exception is VB3: the vertical layering observed in the hydrochemical composition is also reflected in the age distribution. In spring, the age of the upper layer is 5.7 yr, as opposed to 8.2 yr in the case of the bottom layer.

In summer, the tritium concentration of only one sample (VB6) was measured. However, since the $^3$H concentrations measured in the wells do not vary significantly during the investigation, one can approximate the summer tritium concentration by the average $^3$H concentration of all samples taken in May, July and October 1998. Variation of this average summer $^3$H concentration within the 2σ range does not change the calculated age distribution pattern for the summer situation at all. Although a simplification, the assumption of an average summer $^3$H concentration is therefore nevertheless reasonable.

Using the approximated $^3$H concentration of 10.4 ± 2.4 TU for the summer situation, the estimated ages in wells VB1–VB5 are all less than 1.5 yr. Well VB3 is again an exception. The bottom water layer in summer 1998 is much older (18 yr), which agrees well with the high mineralization and emphasizes the close relationship of this bottom water in VB3 to the old groundwater upwelling at VBup. In contrast, the upper water layer of VB3 in summer has an average water age of only 2.8 ± 1.1 yr.

During autumn, all water ages evolve generally towards the winter situation characterized by higher ages. Only VB2 still shows a low water age. This well, which generally exhibits very low ages, is apparently most strongly influenced by near-surface water from the hillslope.
7.5.4 Hydrological system

Based on the information obtained from geochemical and noble gas data, we suggest the following conceptual model describing the hydrological system of the middle floodplain of the Valle di Blenio and its temporal dynamics (Figure 7.8). The aquifer system of the floodplain consists of two different layers: a near-surface zone fed by surface waters (precipitation, snowmelt water, water from tributaries) and a deeper zone containing geochemically evolved groundwater. Although this separation into two vertical aquifer zones is based only on the prevailing hydrochemical water types and the $^3$H-$^3$He water ages, it is consistent with the schematic circulation model of the Acquarossa spring system proposed by Pastorelli et al. (1999). They described the shallow groundwater system in the western part of the Valle di Blenio as a near-surface cold aquifer developed in the Mesozoic sediment cover of the western hillslope of the Blenio valley. The deeper zone of the investigated floodplain aquifer is most likely located in this Mesozoic cover, which results in higher groundwater residence times and a higher degree of mineralization compared to the upper groundwater zone.

The near-surface zone is established in the carbonate-rich detritals and fluvial deposits of the Brenno tributaries and the Brenno itself that overlie the Mesozoic sediment cover in the lower hillslope area. A sharp separation of the two geochemical facies and a definite assignment of these geochemical facies to the two geological facies is not possible and also not intended by this conceptual approach. Although the two aquifer zones are not separated by any aquiclude, the geochemical separation within the aquifer is evident and expresses its presence in the vertical stratification of the two geochemical facies.

Generally, the deeper groundwater samples from wells near the Brenno (e.g., in the bottom layer of VB3) show the influence of the geochemically evolved groundwater facies, while in the more distant boreholes (e.g., VB2) this evolved groundwater component is not obviously present. Looking at the hydrochemical data of the wells near the Brenno (Table 7.1), a seasonal variation in the depth of the transition between the two groundwater facies in accordance to the changes in groundwater levels with a higher position in summer and a lower localization in winter is most likely.
Conceptualized hydrological system of the middle floodplain of Valle di Blenio. The groundwater system is divided into a near-surface level with younger, only slightly mineralized water (recently infiltrated rainwater, snowmelt water; inflow from the upper parts of the hillslope) and a deeper, more highly mineralized zone with older, geochemically evolved groundwater. This distinction is associated with a hydrogeological separation within the aquifer. Note that the surface of the tributary alluvial layer was left white for reasons of clarity.
Pastorelli et al. (1999) also describe a hydrothermal groundwater system in the Valle di Blenio in which deep, relatively permeable, carbonate-rich layers are separated by basement nappes of crystalline rocks, both of them transformed by back-folding processes. Since the crystalline rocks are most likely fractured, the deeper zone of the floodplain aquifer may possibly be influenced by upflowing hydrothermal water from deeper strata. However, the water temperature and the degree of mineralization of the samples analyzed are generally much too low to be interpreted as a mixture of cold, near-surface groundwater and deep thermal waters. Only VBup may show a small portion of such thermal waters. According to Mazor and Vuataz (1990) and Pastorelli et al. (1999), deep and warm groundwater ascends along faults and fractures in the gneissic basement and forms the geothermal spring complex in close vicinity to the Brenno north of Aquarossa. VBup is located very close to this stress zone and can therefore realistically be described in terms of a mixture of a relatively small proportion of an old, mildly geothermal component with younger, fresher groundwater.

Of interest is the water exchange between the groundwater system in the floodplain and the River Brenno. The Brenno acts as the discharge level for the near-surface aquifer, allowing active water exchange between the river and the shallow groundwater, mainly by groundwater exfiltration. In contrast to the shallow groundwater, the deeper and older groundwater zone of the aquifer seems to be rather isolated from the river in that no dilution effect can be evidenced in the deeper groundwater zone. This separation is strongly supported by the geochemical composition of VBup and the deeper water in VB3, which implies that river water infiltration does not exist in the deeper groundwater layer. Considering both aspects, water exchange occurs mainly horizontally between the near-surface groundwater and the river water, whereas the geochemical zoning excludes major vertical water exchange processes.
7.6 Conclusions

The present study attempts to characterize the hydrology of an alpine floodplain, Valle di Blenio, using hydrochemical data and $^3$H-$^3$He water ages. The use of $\text{Mg}^{2+}$ as a tracer of groundwater maturity and the comprehensive interpretation of all 5 noble gases in terms of excess air fractionation enabled appropriate values for the radiogenic $^3\text{He}/^4\text{He}$ ratio and the He/Ne ratio of the excess air component in the studied area to be adopted. The correct determination of these two parameters significantly improves the accuracy of the derived $^3\text{H}$-$^3\text{He}$ water ages.

The interpretation of the hydrochemical data and the calculated water ages indicate a geochemical separation between the River Brenno and its active river bed on the one hand, and the floodplain water in the aquifer and the hillslope on the other. The floodplain water is Ca-HCO$_3^-$-dominated, with two different geochemical facies. The first facies represents a fresh, young summer component of recently infiltrated near-surface water that is present in the floodplain wells, in the Uregn tributary, and in the piezometers PU. The second facies is characterized by older, more evolved, deeper groundwater that is present in the deeper zone of the aquifer and in the upwelling groundwater at VBup. During winter, lower water levels in the floodplain aquifer are associated with a hydrochemical composition of the well samples that tends toward that of the evolved geochemical facies. Water exchange between groundwater and Brenno water occurs mainly as exfiltration of shallow groundwater. The deeper groundwater zone is geochemically separated from the upper groundwater and shows no evidence of river water infiltration.
Acknowledgements

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Chapter 8

Synthesis and outlook

8.1 Excess air formation – Part 2

The experimental investigations of excess air formation in quasi-saturated porous media described in this work, in combination with the kinetic modeling of the dissolved gas transport in the presence of entrapped air bubbles, provide a basis for the development of a physically consistent concept for the generation of excess air (Fig. 8.1).

The initial prerequisite for the formation of excess air is the presence of entrapped air. Entrapped air, which results from vertical water movement, is a regular element in the quasi-saturated aquifer zone. The amount of entrapped air and the size distribution of the entrapped air bubbles depend on the type of substrate and the initial water content of the substrate. Other proposed mechanisms leading to the formation of air bubbles or air pockets in the saturated zone, such as air suction or the downward displacement to the groundwater table of air along with infiltrating water, seem to be rare events that are not capable of generating the omnipresent entrapped air bubbles.

In response to a pressure increase resulting from a rise in the groundwater table, entrapped air bubbles in the quasi-saturated zone tend to dissolve. The degree of supersaturation resulting is influenced by a number of factors. The amount of dissolved gas excess is governed predominantly by the hydrostatic pressure acting on the entrapped air bubbles.
The elemental composition of the excess component is controlled by the flow conditions, by the air-water volume ratio in the pore space, and by the initial size distribution of the entrapped gas bubbles. These parameters efficiently influence whether or not the entrapped air bubbles can be completely dissolved. Furthermore, the initial composition of the dissolved gas component and of the entrapped gas phase control the resulting excess air composition.

The gas excess present immediately after initial dissolution may be subsequently affected by secondary gas exchange processes either across the groundwater table or with a different entrapped gas phase. It is important to note that such types of secondary gas...
Future perspectives are constrained to small hydrostatic overloads; they therefore occur only in the uppermost region of the quasi-saturated zone. Because groundwater samples are usually taken from the core of an aquifer rather than from the region near the water table, excess air patterns measured in groundwater samples can be described well in terms of the unfractionated excess air (UA) concept or the closed-system equilibration (CE) approach. Consequently, groundwater samples with a partial re-equilibration (PR) signature are not expected to be observed in common groundwater studies. According to our conception, the presence of such a diffusively altered supersaturation pattern indicates either water sampling from just beneath the groundwater table or some kind of irregularity in the groundwater flow regime, e.g. the exposure of groundwater to soil air before sampling (Loosli et al., 2000).

8.2 Future perspectives

Based on the results presented, further investigations of the excess air component in groundwater should focus on one or more of the following aspects:

(1) A field-scale investigation of excess air formation.

Although the experiments described here yielded no evidence to indicate that the process of excess air generation might be scale-dependent to any significant degree, a detailed field study would provide useful information regarding the formation of excess air in natural aquifer systems. The increase in substrate heterogeneity that is associated with the transition and scaling-up from laboratory experiments to real soils is an important element in a “real-world” confirmation of the proposed excess air formation concept.

(2) The collection and evaluation of more detailed data of the process of excess air formation.
Two elements can be mentioned here: the bubble size distribution and the analysis of the gas composition in the entrapped air bubbles during the dissolution process. With respect to the first of these topics, relevant problems include the influence of the bubble size distribution on the dissolution processes, the determination of possible varieties of bubble sizes in different substrates, and the possibility of representing a bubble size distribution more efficiently in the kinetic bubble dissolution model.

With respect to the second topic, the possibility of analyzing the composition of the entrapped gas during the process of bubble dissolution can provide some insights into the formation of excess air based on changes in the gas phase composition. The measurement of such changes might yield an independent validation of the results described here that are based on the dissolved gas composition.

(3) Incorporation of other substances into the investigation of excess air. So far we have focused on the application of atmospheric noble gases as hydrological tracers to achieve a more detailed knowledge of excess air formation and of the importance of bubble-mediated gas exchange in groundwater. As a next step, the role of excess air in the exchange of other gaseous compounds like VOCs between soil air and groundwater would be of interest. Is excess air a relevant input pathway for such contaminants into the groundwater, and what would be the effect of a mixture of different volatile organic compounds in the entrapped soil air on the dissolved concentrations of these substances?

These are just a few suggestions for future work in the field of bubble-mediated gas transfer in subsurface hydrology. Since excess air and its role in controlling the gas exchange between groundwater and soil air are still not completely understood, future studies focusing on other scientific research topics are desirable and should aim a better understanding of the excess air phenomenon in groundwater hydrology and ecology.
References


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