



Response of noble gas partial pressures in soil air to oxygen depletion



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ABSTRACT

Soil air composition is known to fluctuate both temporally and spatially. These fluctuations are mainly caused by microbiological activity, leading to oxygen depletion. The exact composition of soil air is of importance to the reconstruction of paleotemperatures using dissolved noble gases in ground water, yet few data exist on the impact of soil air composition changes on the noble gas concentrations. This study documents the evolution of soil air composition, including noble gases, over a period of 17 months at a test site with clay dominated soil in Germany. It confirms that O₂ and CO₂ concentrations within the soil air vary strongly between a minimum of the sum of O₂ and CO₂ of 16.5% and a maximum of 24.5%. Soil air noble gas composition deviated from atmospheric composition as expected, i.e. noble gas concentrations increased when O₂ + CO₂ decreased, and vice versa. The highest observed increase in soil air argon mixing ratio was to 106.4% of the atmospheric air mixing ratio. This maximum increase of noble gas mixing ratios would cause an underestimation of paleotemperatures by 1.5 °C when employing the current models neglecting the response of noble gases to oxygen depletion. Due to the observed annual variation, however, the mean effect is much smaller.

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1. Introduction

The concept of using dissolved noble gases in ground water as proxies for paleotemperature is based on the temperature dependency of gas solubilities in water, the mainly atmospheric source of noble gases in ground water and their chemically inert behavior (Stute and Schlosser, 1993). Within the relevant temperature interval found at ground water recharge areas, the solubility decreases with increasing temperature as described by Henry's Law and the temperature dependent, gas specific Henry constant (Kipfer et al., 2002).

Noble gases enter the water phase by equilibration with air. In the case of ground water recharge this equilibration takes place within the vadose zone between the percolating meteoric water and the local soil atmosphere (Klump et al., 2007). Investigation of the composition and similarity of soil air compared to atmospheric air is the main objective of this study.

Besides equilibration with soil air, dissolved noble gases in ground water can also originate from trapped bubbles of soil air, giving rise to the so-called excess air component (Heaton and Vogel, 1981), i.e. a surplus atmospheric component of dissolved gases in excess of the equilibrium concentrations. For some noble gas isotopes, there also exist other relevant sources than the atmosphere, such as radiogenic ⁴He and ⁴⁰Ar, or tritiogenic ³He. All noble gases have at least one isotope (²⁰Ne, ³⁶Ar and virtually all krypton and xenon isotopes) that is only influenced by atmospheric sources and from which the total atmosphere-derived amount of the respective noble gas can be calculated (Stute and

Schlosser, 1993). Hence the concentrations C_m of the atmospheric noble gases Ne, Ar, Kr, and Xe found in actual ground waters are the sum of two atmospheric sources that introduce noble gases into the water:

$$C_m = C_{eq} + C_{ex} \quad (1)$$

where m stands for measured, eq for atmospheric equilibrium, and ex for excess air. The temperature information is contained in the equilibrium component via the temperature dependence of the solubilities. A correct description of the excess air component is therefore required to calculate a noble gas temperature (NGT) from a set of measured dissolved atmospheric noble gas concentrations.

To account for the effect of excess air on measured noble gas concentrations, various models have been developed and applied to ground water samples, allowing to reconstruct paleotemperature records (Kipfer et al., 2002; Aeschbach-Hertig and Solomon, 2012). In some cases, a depletion of atmospheric noble gas concentrations relative to equilibrium has been observed and also for this case of degassing, different models have been proposed (Aeschbach-Hertig et al., 2008). The classical explanation for excess air is that bubbles of soil air in fine pores get trapped by infiltrating ground water and are transported into the saturated zone, where they are completely dissolved under increased hydrostatic pressure (Heaton and Vogel, 1981). This leads to an injection of soil gas into the ground water, and usually the additional assumption has been made that this soil gas has the same noble gas composition as atmospheric air, thus the excess air has atmospheric composition (Kipfer et al., 2002).

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However, in many studies of dissolved noble gases in ground water, it has been found that the excess air component is fractionated relative to atmospheric air, with the heavy noble gases being enriched compared to the lighter ones with respect to the composition of air. This effect was first described by Stute et al. (1995) and explained by partial re-equilibration of the ground water after an initial formation of excess air. Later it has been shown that this model does not accurately describe many noble gas data sets (Aeschbach-Hertig et al., 1999; Ballentine and Hall, 1999). A more realistic picture of the processes forming excess air is that soil air is trapped during water table rises and the entrapped air is then only partially dissolved due to insufficient hydrostatic pressure. An equilibration between entrapped air bubbles and the surrounding, initially equilibrated water in a closed system also leads to fractionated excess air and was found to be quite successful in explaining observed noble gas patterns (Aeschbach-Hertig et al., 2000).

NGTs derived using the above models for excess air from shallow wells with modern ground water should usually reflect the soil temperature in the recharge area at the ground water table, where the final equilibration between the water and the soil air takes place. Ideally, this water table temperature (WTT) and the corresponding NGT represent the mean annual air temperature (MAAT) of the infiltration region at the time of recharge. However, in a noble gas paleotemperature study in southern Michigan, Ma et al. (2004) found that NGTs from modern ground waters displayed a systematic underestimation of MAAT by several degrees Celsius. This cold bias of NGTs was confirmed also with respect to WTT in a further study in the same region dedicated to the shallow ground water (Hall et al., 2005). In order to explain the deviation between NGT and WTT (or MAAT in that case), these authors proposed the oxygen depletion or OD model for the formation of excess air. It abandons the assumption that equilibration within the soil takes place between water and atmospherically composed air (Stute and Schlosser, 1993). It was argued that biological processes depleting O₂ and producing CO₂, combined with CO₂ removal from the soil air due to its high solubility in water, may lead to a pressure deficit that is compensated by rising partial pressures of the remaining gases (Hall et al., 2005).

While it is known that the processes of O₂ depletion and CO₂ dissolution can occur in soils and may lead to a deficit in the sum of the partial pressures of O₂ and CO₂, it has usually been assumed that this effect is only significant under special conditions and thus generally of minor relevance for the NGT method (Stute and Schlosser, 1993). Moreover, it has never been experimentally verified that a depletion of the sum of O₂ and CO₂ does indeed influence the partial pressures of the noble gases in soil air. In a recent study Hall et al. (2012) have observed seasonal variations in dissolved oxygen and noble gas concentrations in ground water but did not conduct direct measurements of the soil air. The intent of this study is to create a soil air composition record to investigate whether and under which conditions the proposed oxygen depletion mechanism occurs and whether it has a significant effect on the noble gas composition of soil air.

2. Methods

The site for soil air sampling was specifically constructed for this study and is located at N 49°25.050, E 8°40.496 on the campus of Heidelberg University, near the eastern margin of the sedimentary plain of the Upper Rhine Graben. The sediments in this region form several sandy aquifers separated by silt and clay layers. The ground water table of the upper unconfined aquifer at the site location is at a depth of 14 m. The mean annual precipitation in the region is around 800 mm, which is expected to produce considerable recharge at the flat study site with little if any surface runoff.

In June 2010, a single borehole with a diameter of 6 cm and a depth of 6 m was drilled in clay dominated soil covered by lawn. Sampling tubes (Tygon® vacuum tubing) of lengths 2, 4 and 6 m were lowered into the hole, which was subsequently refilled with slurry. The slurry

consisted of material excavated from the borehole to keep the disturbance of the natural conditions as low as possible. Sampling did not commence until a month passed to let the refilled borehole settle. Each sampling tube has a screen of 10 cm length at the lower end and can be accessed separately above ground. Additionally, temperature sensors with data loggers were placed at 2.5, 1.0 and 0.1 m depth.

Proper sealing against atmospheric contamination and air exchange along the sampling tubes between the different depth screens was monitored for by measuring ²²⁰Rn and ²²²Rn concentrations, as well as CO₂- and O₂-concentration evolution during pumping for sample collection. The radon measurements were of a qualitative nature and were used exclusively as a tool to identify atmospheric leakage. The data showed stable values for each depth over the course of the first 9 months of sampling, well above atmospheric concentrations, indicating that no atmospheric contamination took place. Once proper borehole sealing was ensured, the measurements were discontinued to minimize the amount of soil air being removed by each sampling.

CO₂ and O₂ concentrations in soil air were measured as volume or mole fractions (in %) on-site using a handheld device (Geotech BM2000 Biogas Monitor). Since the device was only available as of February 2011, previously collected noble gas samples lack corresponding CO₂ and O₂ data. O₂ was measured electrochemically with an accuracy (in absolute volume fractions) of ±1.0%, while CO₂ was measured by IR-absorption with an accuracy of ±0.5% in the concentration range of 0–5% and ±1.0% for concentrations from 5–15%. ²²⁰Rn and ²²²Rn was measured using a DurrIDGE RAD7 to rule out atmospheric contamination.

The noble gas samples were collected by pumping soil air for 2–30 min with a pump rate of approximately 0.5 l/min through thin copper tubes (inner diameter: 4 mm). Based on literature data on clay soil pore space volume, pumping time and rate, the evacuated soil volume was estimated, leading to a resulting depth range of sampling of around ±0.2 m. The copper tubes were closed airtight with a pneumatic plier, resulting in samples of about 1.5 cm³ volume at atmospheric pressure. Supplementary atmospheric air samples were collected in the same way for reference.

The noble gas samples were measured using a GV Instruments MM5400 mass spectrometer (Friedrich, 2007), using methods similar to those described by Beyerle et al. (2000). Exact gas amounts were determined by expanding the samples into a known volume within the mass spectrometer's preparation line and measuring the pressure in this volume. The effect of saturation water vapor pressure on soil air partial pressures was accounted for by assuming saturation of soil air with water vapor, all calculations of gas mixing ratios reflect dry air fractions. The analyzed noble gas isotopes were ³He, ⁴He, ²⁰Ne, ²²Ne, ³⁶Ar, ⁴⁰Ar, ⁸⁴Kr and ¹³²Xe. We analyzed the major isotopes of the noble gases He, Ne, Ar, Kr and Xenon, as well as the ratios ³He/⁴He, ²⁰Ne/²²Ne and ⁴⁰Ar/³⁶Ar. Measured peak heights were converted to gas amounts by comparison with an atmospheric calibration standard of known composition and size. Using the sample's total gas amount and literature values (Porcelli et al., 2002) on the abundance of atmospheric noble gases, the deviation of the sample's noble gas concentration from atmospheric air was calculated.

Noble gas data from samples of atmospheric air showed an underestimation of all noble gases except xenon by roughly 2% relative to literature data for all samples measured at the mass spectrometer before June 2011. The cause was identified as a systematic error in the measurement of the inlet pressure of the preparation line, which was subsequently dealt with by improving the gas preparation procedure. The affected soil air samples were corrected using the mean offset of each noble gas isotope, determined from comparison of the atmospheric air sample data with literature data.

The sampling timeframe discussed in this paper covers a timespan of 17 months, starting in August 2010. An unusual and extended dry period in the spring of 2011 caused a stagnation of biological activity (Schimmel et al., 1999). In order to stimulate biological activity and related changes in soil air, it was decided to interrupt the natural state

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