



ORIGINAL ARTICLE

Noble gases in aquitard provide insight into underlying subsurface stratigraphy and free gas formation

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Abstract

Biogeochemical gas production resulting in free gas phase formation can severely affect groundwater and solute transport in aquifers. Such gas–water interactions are important in aquifers affected by geogenic As, which are commonly associated with biogeochemical CH₄ production. Additionally, the influence of aquitards on As concentrations in contaminated aquifers has recently been challenged. These observations prompted the analysis through a heterogeneous aquitard overlying a high CH₄–gas-producing zone of an As-contaminated aquifer. A sediment core taken through the aquitard was analyzed for noble gases to assess how the aquitard physically contributes to the underlying gas production. Results reveal that the aquitard pore space is unsaturated in two separate layers resulting in hanging pore water constrained by an air-like gas phase. This interlayering of unsaturated and saturated zones identifies the aquitard's stratigraphy as key in determining hydrostatic pressure—a main control of free gas formation (i.e., CH₄) in the underlying aquifer. The partly unsaturated conditions reduce the hydrostatic pressure by 30% compared with fully saturated conditions. To our knowledge, this is the first study applying noble gases to examine the influence of an aquitard's physical state on gas production in an underlying aquifer. Further, such partly unsaturated sediment layers of low conductivity might provide preferential pathways for periodic water flow, fostering aquitard–aquifer solute transport. Groundwater samples additionally collected throughout the study site confirm more widespread degassing than previously reported. Up to 90% of the expected atmospheric noble gas concentrations is lost from groundwater immediately below the investigated sediment core.

1 | INTRODUCTION

Noble gases are increasingly being applied as reliable geochemical tracers in aquatic sediments to investigate the dynamics of fluids and gases in the sediment pore space.

Such aquatic sediments include aquitards (Hendry et al., 2005; Sheldon et al., 2003), the quasi-saturated zone (Jones et al., 2014; Pérotin et al., 2021), and lacustrine and oceanic sediments (Brennwald et al., 2005, 2013; Horstmann et al., 2021; Strassmann et al., 2005; Tomonaga et al., 2014; Tyroller et al., 2021). However, despite recent methodological advances

Abbreviations: ASW, air saturated water.

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simplifying the extraction and analysis of the noble gases from sediment pore water (Brennwald et al., 2003; Hendry et al., 2005; Tomonaga et al., 2011), there are a limited number of studies applying noble gases as tracers specifically in aquitards and the quasi-saturated zone.

The study of fluids, gases, and gas transport in aquitards is particularly relevant in cases where adjacent aquifers are highly contaminated. Arsenic is serious contaminant affecting many aquifers around the world that can be influenced by aquifer–aquitard exchange. Such exchange is increasingly being challenged as a contributing factor toward As mobilization in contaminated aquifers, with several studies either confirming or anticipating a significant input or exchange of solutes at the aquitard–aquifer interface (McMahon & Chapelle, 1991; McMahon, 2001; Mihajlov et al., 2020; Stopelli et al., 2020, 2021). This exchange further offers to be a contributing explanation toward the particularly high and heterogeneous As concentrations often observed in affected aquifers (e.g., Smedley & Kinniburgh, 2002; Van Geen et al., 2006; Wallis et al., 2020).

Simultaneously, As has been observed to be associated with the biogeochemical production of methane (CH_4) in aquifers under highly reducing conditions. The correlation between As and CH_4 in many contaminated aquifers is prominent (Dowling et al., 2002; Jessen et al., 2008; Postma et al., 2007; Stopelli et al., 2021), with promising explanations for the correlation identified recently in several studies (Glodowska, Stopelli, Schneider, Rath, et al., 2020; Lightfoot et al., 2022; Pienkowska et al., 2021). Where the biogeochemical gas production of any gas species (e.g., CH_4 , nitrogen [N_2], carbon dioxide [CO_2]) surpasses the hydrostatic pressure, a free gas phase (bubbles) in the pore space of the aquifer matrix may form (Amos & Mayer, 2006; Andrews et al., 1991; Blicher-Mathiesen et al., 1998; Fry et al., 1997; Revesz et al., 1995; Ryan et al., 2000). Such entrapped gas bubbles can have severe consequences for the hydrogeological dynamics of groundwater (Amos & Mayer, 2006; Baird & Waldron, 2003; Lightfoot et al., 2022; Reynolds et al., 1992; Yager & Fountain, 2001), significantly reducing the hydraulic conductivity in a variety of aquatic environments (Amos & Mayer, 2006; Fry et al., 1997; Heilweil et al., 2004; Ryan et al., 2000) and, more critically, causing partial hydraulic isolation of the gas-producing zone. Further, such in-aquifer biogeochemical gas production occurring near the water table has been observed to migrate into the quasi-saturated zone, proving to be an important pathway for carbon and CH_4 exchange and transport (Jones et al., 2014). The influence such gas (bubble) production has on the solute dynamics both in groundwater and in the quasi-saturated zone is therefore highly relevant in contaminated aquifers where groundwater transport and the mechanisms governing contaminant dynamics are critical to assess.

In this study we investigate the physical controls overlying a specific CH_4 -producing zone in the studied aquifer where

Core Idea

- Noble gases distinguish between saturated and unsaturated sediments in a heterogeneous aquitard.
- Unsaturated sediments reduce the hydrostatic pressure on an underlying aquifer.
- Free CH_4 gas formation in underlying aquifer is enhanced by the reduced hydrostatic pressure.
- Widespread degassing associated with high CH_4 concentrations are observed in groundwater.

severe groundwater degassing is observed. Since the CH_4 -producing zone is located directly below an aquitard–aquifer interface (Stopelli et al., 2021; van Geen et al., 2013), water and gas exchange through the overlying aquitard is key to analyze. Specifically, the main objective is to understand how the aquitard might physically contribute to the gas dynamics and CH_4 production in the underlying aquifer.

Assessment of the aquitard is accomplished by analyzing the noble gases in the aquitard pore space. The choice of noble gases as tracers is relevant here because they are naturally existing in the water cycle, are nonreactive, and are solely sensitive to physical processes (Aeschbach-Hertig & Solomon, 2013; Kipfer et al., 2002). To our knowledge, this is the first study that uses the unique properties of noble gases to examine the influence of the physical state of an aquitard on an underlying aquifer, which is highly impacted with As and concomitant CH_4 production. In addition, our analysis will provide a framework on which the biogeochemical exchange processes between the aquitard and aquifer can be developed.

Noble gases are additionally analyzed in the groundwater of the underlying aquifer both at the location selected for aquitard porewater analysis and for the wider study site area to clarify the extent of degassing at the field site.

1.1 | Noble gases as tracers

Noble gases are applied as natural tracers in aquatic systems where it is necessary to differentiate between biogeochemical reactions and physical transport and exchange processes (e.g., Blicher-Mathiesen et al., 1998; Kipfer et al., 2002; Mächler et al., 2012; Popp et al., 2020; Stanley & Jenkins, 2013). However, to gain a relevant interpretation of what physical processes may have occurred, measured concentrations of a site-specific sample must be compared with the expected air saturated water (ASW) concentrations for that site. Since noble gases enter the water cycle through exchange at an air–water interface, ASW concentrations are generally derived from the last moment the water parcel was in

contact with the atmosphere. Therefore, the ASW concentrations in groundwaters are controlled by the local prevailing environmental conditions: water temperature, salinity, and altitude (Supplemental Table S1) (Aeschbach-Hertig & Solomon, 2013; Kipfer et al., 2002).

Groundwater samples exhibiting deviations from ASW concentrations allow identification of which physical processes (i.e., excess air formation, degassing, or radiogenic accumulation (of the radiogenic noble gases) may have fractionated the gases in the local groundwater. Excess air is produced when pockets of air are trapped in the quasi-saturated zone, and, as the water table rises, an increased hydrostatic pressure forces the noble gases present in the trapped air pockets to dissolve into the groundwater (Aeschbach-Hertig et al., 2002, 2008; Kipfer et al., 2002). Excess air is thus often associated with aquifers subject to frequent fluctuations in the water table (Aeschbach-Hertig et al., 2002; Klump et al., 2007, 2008; Mächler et al., 2013). Degassing, contrarily, is associated with a characteristic depletion of noble gases in groundwater (e.g., Aeschbach-Hertig et al., 2008; Brennwald et al., 2005; Heilweil et al., 2004; Tyroller et al., 2021; Visser et al., 2007). This depletion occurs due to the repartitioning of the original noble gases dissolved in the water phase into a newly formed gas phase, which subsequently escapes the aquatic environment under study leaving behind noble gas depleted groundwater. Such newly formed free gas phases (or gas bubbles) below the water table are generally the result of biogeochemical reactions and are not to be confused with entrapped (excess) air bubbles in the quasi-saturated zone.

Accumulation of the radiogenic noble gases is most frequently observed in the helium (He) isotopes (^3He , ^4He) and can inform us about the residence times of groundwaters in aquifers and also in the porewaters of more consolidated sediments (Kipfer et al., 2002; Solomon et al., 1996; Strauch, 2014). Helium-4 (^4He) accumulates as a consequence of the radioactive decay of uranium and thorium naturally abundant in the aquifer and aquitard matrices and is representative of longer groundwater and porewater residence times (range of 10^3 – 10^8 yr) (Solomon et al., 1996). Tritogenic ^3He , produced via the radioactive decay of tritium (^3H), enters a water body at the air–water interface as tritiated water and is applied in the case that shorter groundwater residence times (<70 yr) are anticipated (Gilmore et al., 2021; Kipfer et al., 2002; Schlosser et al., 1988). While both ^3H and the tritogenic ^3He concentrations are required for dating young groundwaters, some qualitative information can be inferred from the ^3H concentrations alone. After the specific water parcel is no longer in exchange with the atmosphere, the ^3H concentration in a water parcel will exponentially decrease over time. Higher relative ^3H concentrations in groundwater of a specific field site thus indicates shorter groundwater residence times because less time has passed for ^3H to decay into tritogenic ^3He . Alternatively, ^3H may also be understood in terms

of a higher fraction of post-bomb water present in a particular groundwater parcel (e.g., Lamontagne et al., 2021).

2 | MATERIALS AND METHODS

2.1 | Geological setting and field site

Van Phuc is a small village situated inside a meander of the Red River (Figure 1) deltaic region around 15 km southeast of Hanoi City (Vietnam). Previously reported high and spatially heterogeneous As and oversaturated CH_4 concentrations in groundwater (Glodowska et al., 2021; Lightfoot et al., 2022; Stopelli et al., 2020, 2021), in conjunction with a heterogeneous aquitard capping the aquifer system, made the village ideally suited to study the influence of aquitard properties on the underlying aquifer. Such aquifer characteristics are also typical of many other As-contaminated field sites, making the Van Phuc aquifers appealing to study in the worldwide concern of As groundwater contamination particularly because the site is also easily accessible (e.g., Berg et al., 2008; Eiche et al., 2008, 2017; Glodowska, Stopelli, Schneider, Lightfoot, et al., 2020; Glodowska, Stopelli, Schneider, Rath, 2020; Glodowska 2021; Kontny et al., 2021; Lightfoot et al., 2022; Nghiem et al., 2020; Stahl et al., 2016; Stopelli et al., 2020, 2021; van Geen et al., 2013).

Underlying the southeast of the village is a young (Holocene) aquifer associated with high As concentrations of up to $500 \mu\text{g L}^{-1}$ (Stopelli et al., 2021). In the northwest of the village, an older (Pleistocene) aquifer is present (Eiche et al., 2008) with low or no As concentrations, $<10 \mu\text{g L}^{-1}$, as given by the World Health Organization as the safe limit for As in drinking water. Groundwater flows in the direction from the younger aquifer to the older aquifer (or, southeast to northwest along the transect in Figure 1), which is in reverse to the natural groundwater flow (Berg et al., 2008; Stahl et al., 2016; van Geen et al., 2013; Wallis et al., 2020). This flow reversal is a consequence of the large-scale abstraction of groundwater by the municipal waterworks in Hanoi and applies year-round (Stahl et al., 2016) in both dry (November–April) and wet (May–September) seasons. As a result of the enhanced groundwater extraction, water from the Red River began to infiltrate into the Holocene aquifer >50 yr ago (van Geen et al., 2013; Wallis et al., 2020).

Capping the studied aquifers, is a silt–clay aquitard that varies in thickness between 10 and 23 m (Figure 1) (Eiche et al., 2008, 2017). Previous drilling campaigns (Eiche et al., 2008, 2017) have established that the aquitard in the northwest of the village, that is, close to Well 15 in Figure 1, extends down to approximately 23 m in depth and contains a high proportion of silt–clay sediments of up to 75%. In contrast, the same aquitard in the southeast of Van Phuc, that is, around

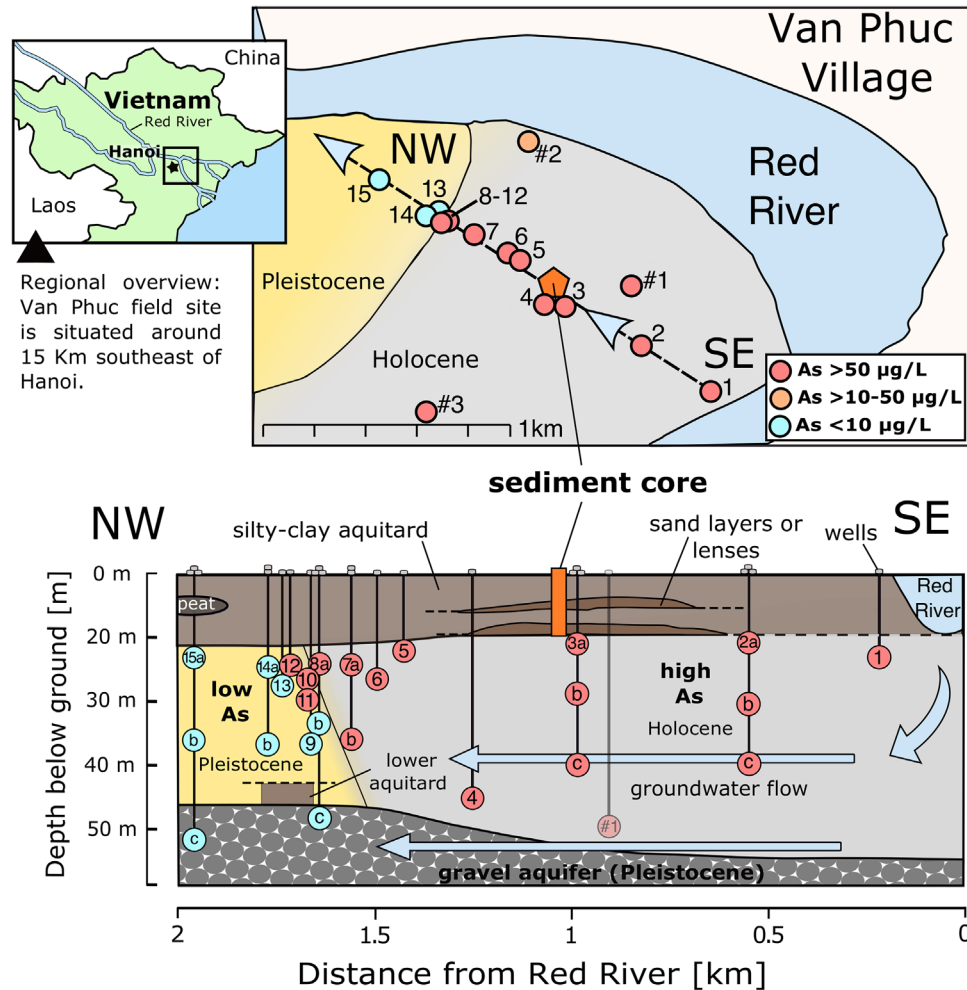


FIGURE 1 Upper: Aerial schematic of Van Phuc village, around 15 km SE of Hanoi. The sediment core was taken near the local health clinic ($20^{\circ}55'04.1''$ N, $105^{\circ}53'54.3''$ E; orange pentagon). Sampled wells are numbered circles showing groundwater with high ($>50 \mu\text{g L}^{-1}$; dark pink), intermediate (orange) and low ($<10 \mu\text{g L}^{-1}$; light blue) As concentrations. Wells with '#' are those situated outside of the transect line. Lower: Subsurface profile along the transect line, whereby numbered sampling wells show approximate well screen depths (see Supplemental Table S3 for specific well screen depths and GPS co-ordinates). The location of the sediment core (rectangle) is highlighted. Dashed lines indicate uncertainty in how far layers extend through the aquitard and aquifer. A hydraulically connected gravel aquifer of Pleistocene age underlies both upper sandy aquifers. Adapted from Lightfoot et al. (2022)

200 m downstream of Well 3 in Figure 1, reaches a depth of approximately 10 m and has been identified to be highly heterogeneous (Eiche et al., 2008, 2017; Stopelli et al., 2020; Van Geen et al., 2013), whereby, at depths of 4 and 7 m, the sand content increases to 25 and 50%, respectively. Subsequently, between depths of 10 and 20 m, the sand content fluctuates up to a maximum of 80% (Supplemental Figure S2). In addition, the aquitard has been shown to contain interbedded layers rich in peat and organic matter (Eiche et al., 2017; Tanabe et al., 2003).

Given the sedimentological heterogeneity of the aquitard, previous studies have questioned whether substantial solute input may be a possible factor contributing to some of the highest As concentrations in the aquifer ($385\text{--}500 \mu\text{g L}^{-1}$) (Berg et al., 2008; Eiche et al., 2008; Stopelli et al., 2021). The

speculation that a hydrological connection between aquitard and aquifer exists is additionally supported by stable isotope data from sampled groundwater wells (Stopelli et al., 2020). The stable isotopes reveal that groundwater samples lie at various points along a mixing line in which end members were Red River water and pond water, whereby such ponds are inlaid into the overlying aquitard. Results implied some hydraulic connection between these overlying ponds and the aquifer through preferential flow paths in the aquitard (Stopelli et al., 2020, 2021).

In our study, the aquitard situated below the health clinic of the village ($20^{\circ}55'04.1''$ N, $105^{\circ}53'54.3''$ E) was the targeted location for pore analysis since the sediments in the upper aquitard were predicted to be highly heterogeneous (as anticipated from Eiche et al., 2008, 2017), while

underlying groundwater is observed to contain simultaneously high As and CH₄ concentrations (Glodowska et al., 2021; Stopelli et al., 2021).

2.2 | Arsenic mobilization and retardation in Van Phuc

The general and commonly accepted mechanism controlling geogenic As release in aquifers, such as that underlying Van Phuc, is by microbial reduction of iron-oxyhydroxides (Anawar et al., 2006; Berg et al., 2007; McArthur et al., 2001; Nickson et al., 2000; Ravenscroft et al., 2011). Organic carbon is vital to facilitate the mobilizing reaction; however, its origin is not always clear. At our study site, the riverbed has been previously identified as a key contributor to the source of dissolved As since the groundwater flow was reversed (Wallis et al., 2020). The high spatial heterogeneity of As concentrations (which become particularly high in wells close to the aquifer–aquitard interface), however, has pointed to an additional mechanism responsible for mobilized As (Berg et al., 2008; Eiche et al., 2008; Stopelli et al., 2021). The overlying aquitard, being rich in organic matter, is therefore anticipated to be a potential carbon source for mobilizing As in wells close to the aquifer–aquitard interface.

Concerns for the potentially highly contaminated groundwater from the young aquifer to affect the pristine As-free groundwater of the older aquifer (Figure 1) have been lessened since the observation that As is retarded at the lithological fronts (Van Geen et al., 2013). This retardation is mainly as a result of As sorbing to the prevailing secondary iron minerals [i.e., microcrystalline iron-(oxyhydr) oxides] (Rathi et al., 2017). Until now, the retardation of As at this interface has remained relatively stable (Stopelli et al., 2020) although hydrogeochemical changes in the composition of groundwater in the Pleistocene aquifer have been reported.

2.3 | Sampling and sample processing: Porewater from sediment core

A field campaign was undertaken in November 2018 during which a sediment core through the upper aquitard was acquired near the local health clinic (Figure 1). Coring was carried out via dry hammer drilling in combination with stainless steel liners. Each section of the liner containing the core was brought to the surface and cut into smaller sections of approximately 20 cm in length. The smaller sections (still contained by the steel liner) could then fit into a specially designed press for subsequent sediment transfer into copper tubes (Brennwald et al., 2003; Tomonaga et al., 2014). Sediment transfer into the copper tubes is managed immediately after core recovery to minimize air contamination. The press

is designed such that the sediment sample in the smaller liner section can be pushed into a copper tube with the aid of a specifically made piston that perfectly fits the width of the steel liner (Supplemental Figure S1.1). A steel tube, which acts as a transfer port to deliver the freshly attained sediments from the liner into the copper tube, is pushed 5 cm deep into the sediment section to again minimize air contamination.

The sediment is then flushed (squeezed) continuously through a fixed copper tube of approximately 60 cm in length before the copper tube is clamped airtight at both ends and removed from the press ready for transportation. For our study, a sampling resolution of 0.5–1 m was achieved for depths between 6 and 15 m through the sediment core. Further details, specifically on the sampling procedure of sediments for noble gas analysis, can be found in Tomonaga et al. (2011, 2014) where the same squeezing method was applied as adapted from the original procedure outlined in Brennwald et al. (2003).

The 60-cm copper tubes containing fresh sediment samples for porewater analysis (Supplemental Figure S1.1) were shipped to our laboratory in Switzerland. Subsequently, these samples were clamped and cut into smaller aliquots of 10 cm for centrifugation. Centrifugation is a vital step in processing, as it separates the pore water from the sediment without atmospheric contamination (see Tomonaga et al., 2011). Once centrifuged, samples were again pinched off using clamps at the interface between the pore water and sediment. To know exactly where the sediment–porewater interface is, duplicate samples are routinely centrifuged and opened (for further details see Tomonaga et al., 2011). The prepared smaller water sample (approximately 0.5–1 g) is subsequently measured for noble gases using the same analytical protocol as for usual groundwater samples (45 g, see below; Beyerle et al., 2000).

2.4 | Sampling: Groundwater

Groundwater samples were taken at both pre-existing and newly constructed wells throughout the field site (Figure 1). While the aim was to analyze noble gas concentrations in the groundwater immediately below the drilled core, samples were taken at all accessible well locations of the study site, including seven newly installed wells, for a complete understanding of the subsurface noble gas concentrations in groundwater. The new wells (2a–c, 3a–c, and 5), were sampled around 4 mo after installation. Installation took place at the same time as the sediment coring in November 2018. All other wells were sampled in November 2018.

In total, 28 groundwater wells were sampled for noble gas (He, Ne, Ar, Kr, and Xe) and tritium analysis. For each well, groundwater was pumped to the surface for 10 min using a submersible electric pump (to avoid degassing) before sampling. The pump was connected to one end of a copper tube

via transparent rubber tubing with tightly clamped connections to avoid atmospheric contamination. The copper tube was mounted on an aluminum rack for support with two fixed stainless steel Swagelok clamps situated at either end of the copper tube (1 m apart) and able to contain approximately 45 g of groundwater. After flushing the copper tube, the clamps were sealed airtight, and the sample was transported back to Switzerland to be measured for noble gases via the static mass spectrometer at the ETH noble gas laboratory in Zurich. The usual and well-accepted measuring protocol detailing the noble gas extraction, separation, measurement, and mass spectrometric analysis of noble gases and tritium (via in-growth of ^3He) in water samples is described in Beyerle et al. (2000). To further elucidate that degassing upon sampling was not occurring, a comparison with a previous and robust data set obtained directly in the field (Lightfoot et al., 2022) by continuous in-situ gas measurements using a portable mass spectrometer (or miniRUEDI) (Brennwald et al., 2016) was made for gases Ar and Kr (Supplemental Figure S4). In addition, CH_4 concentrations were sampled during the same November 2018 field campaign and are reported in Stopelli et al. (2021).

We note that while the previously reported data set for Ar and Kr (Lightfoot et al., 2022) was highly reliable, groundwater analysis from this previous study did not include data from several of the more recently installed wells critical to our study's conclusions, specifically Wells 3a and 3b, which are situated below the investigated sediment core. Further, at the time of the field campaign in 2018, Ne, Xe, and tritium could not be quantified with such on-site analysis as applied in Lightfoot et al. (2022).

3 | RESULTS AND DISCUSSION

3.1 | Aquitard pore space: Saturated vs. unsaturated conditions

Noble gas data from the pore space of the aquitard sediment core (i.e., as prepared from the small copper tube aliquots) is plotted in Figure 2, where total Ar and Ne amounts (Supplemental Table S2) have both been normalized to the total Kr amount for each sample. In the plot, two distinct clusters are observed. Notably, samples in the lower cluster, S (saturated water layer) have noble gas ratios close to ASW ratios, implying these samples are situated in parts of the aquitard where water-saturated conditions prevail. In contrast, samples in the upper cluster, U (unsaturated water layer) show noble gas ratios much closer to the ratio in air, suggesting that the pore space comprises of a gas phase with air-like noble gas ratios. Visual observations of gas bubbles in the sediment samples situated in the unsaturated cluster (Supplemental Figure S1.2) further support the interpretation

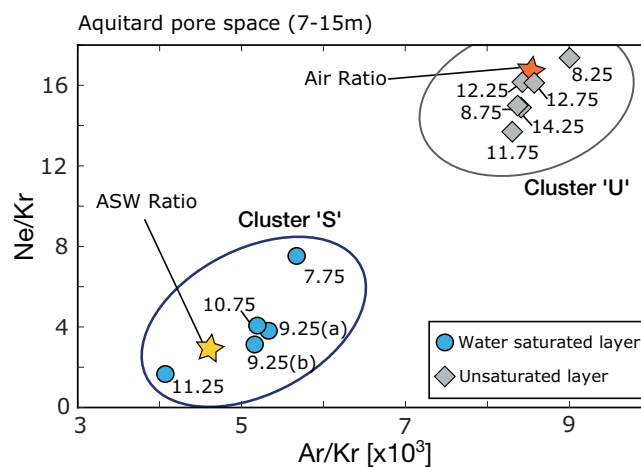


FIGURE 2 The Ne/Kr vs. Ar/Kr ratios for different depths (numbers next to data points indicate the sample depth in meters) throughout the aquitard sediment core. Two distinct clusters are recognized: those situated in saturated (S) pore space and those in the unsaturated (U) pore space. Stars indicate the noble gas ratios in air (dark orange) and air saturated water (ASW; light yellow). For all samples, errors are smaller than the data point and are quoted individually in Supplemental Table S1. Overall, standard 1σ errors for individual Ne, Ar, and Kr amounts are $<3\%$, which are derived from the reproducibility of standard measurements and the uncertainty in the regression algorithm fitted to the signal (current) at the time of analysis (for details see Beyerle et al., 2000)

of unsaturated conditions. Gas bubbles were not observed in sediment samples from the saturated cluster.

Notably, some elemental fractionation in Figure 2 is observed in samples from both saturated and unsaturated layers. The observed fractionation is likely the result of mixing between the two components, that is, ASW and air, in response to varying degrees of quasi-saturation through the sediment cores pore space. For the saturated cluster samples, this mixing trend is illustrated similar to an excess air component in groundwater.

For the unsaturated cluster samples, there is the additional possibility that such fractionation is the result of a pressure gradient induced by different biogeochemical reactions (e.g., methanogenesis underlying CH_4 oxidation, see Jones et al., 2014). However, since analysis of the reactive gas species, such as CH_4 and CO_2 , in the gas phase of the quasi-saturated zone was not feasible in this study, it cannot be concluded that such pressure gradients drive the observed fractionation pattern.

3.2 | Aquitard structure and spatial distribution of helium isotopes

Figure 3 shows the $^3\text{He}/^4\text{He}$ ratio plotted against depth through the aquitard in which a layering is also illustrated

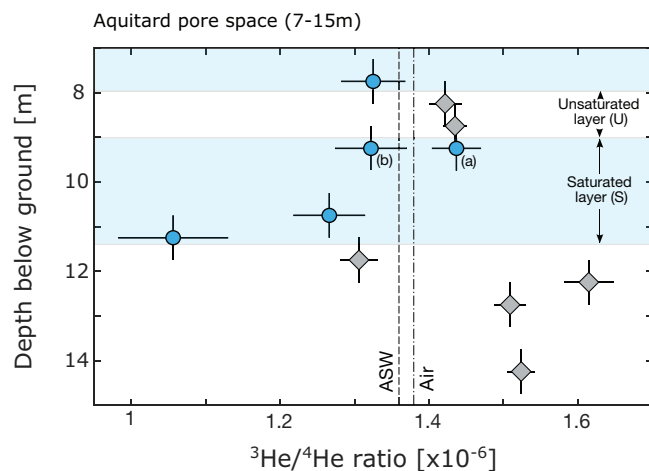


FIGURE 3 Plot of $^3\text{He}/^4\text{He}$ ratios vs. depth through the investigated sediment core. Saturated (blue circles) and unsaturated (grey diamonds) samples are illustrated along with shading of the saturated 'layers' according to the identified clusters in Figure 2. A duplicate sample was taken at 9.25 m, labelled (a) and (b). The left vertical dashed line indicates the expected $^3\text{He}/^4\text{He}$ ratio in air saturated water (ASW), whereas the right dashed line shows the corresponding ratio in air. The standard 1σ error on the $^3\text{He}/^4\text{He}$ ratio overall is $<7\%$. The absolute errors are quoted in Supplemental Table S2

of the saturated and unsaturated pore space as based on the observed clusters in Figure 2. Two unsaturated layers, in fact, exist in the upper 15 m of the sediment core. Notably, the sand content and hydraulic conductivity have been shown to also increase in close proximity to these unsaturated layers as observed in a sediment core taken ~ 200 m downstream from our investigated core (Eiche et al., 2008) (Supplemental Figure S2). Nearly all samples in the unsaturated cluster show $^3\text{He}/^4\text{He}$ ratios higher than the air ratio (1.38×10^{-6}) (Clarke et al., 1976), while most samples in the saturated cluster show $^3\text{He}/^4\text{He}$ ratios below ASW (1.36×10^{-6}) (Weiss, 1970). Exceptions are two samples close to the saturated–unsaturated interfaces (at depths 9.25 and 11.75 m).

The particularly low $^3\text{He}/^4\text{He}$ ratio in the sample at 11.25 m (approximately 20% lower than the ASW ratio) most clearly indicates the presence of radiogenic ^4He , which is additionally supported by the low Ne/He ratio illustrated in Supplemental Figure S3. Supplemental Figure S3 also confirms the presence of radiogenic ^4He to be present in other saturated cluster samples (depths 10.75 and 7.75 m). Further evidence suggesting presence of radiogenic He is provided by the fact that $^{20}\text{Ne}/^{22}\text{Ne}$ ratios do not substantially fractionate from air and ASW ratios (Supplemental Table S2.2). Nonfractionation of the $^{20}\text{Ne}/^{22}\text{Ne}$ ratios also indicates that partitioning of gases at the gas–water interface is equilibrium controlled. Generally, the amount of ^4He present in the pore space will increase as contact time with the surrounding matrix increases as also observed in the aquitard porewater of previous studies (e.g., Hendry et al., 2005; Sheldon et al., 2003).

The lower unsaturated layer has several samples with an enriched $^3\text{He}/^4\text{He}$ ratio (10–15% higher than the air ratio). Thus, particularly in the lower part (from around a depth of 10 m onward) of the sediment core, the He isotopes, and therefore also the $^3\text{He}/^4\text{He}$ ratio of the aquitard's pore space, appears to be influenced by the aquitard's sedimentological layering. Whereby variations in the $^3\text{He}/^4\text{He}$ ratios are explained either by accumulation of radiogenic ^4He in the more confined (saturated) sediments or by transport of tritogenic ^3He from across the water table (Gilmore et al., 2021; Solomon & Cook, 2000) into the lower unsaturated sediments. Further, the sample at 11.75 m, close to the lower saturated–unsaturated interface, shows a $^3\text{He}/^4\text{He}$ ratio between that of the saturated and unsaturated layers, implying He exchange across the saturated–unsaturated boundary.

While the lower confined saturated layer implies that any significant solute input into the underlying aquifer is more likely controlled by laterally connected layers or lenses of higher conductivity in the overlying aquitard, the variations in the $^3\text{He}/^4\text{He}$ ratios, particularly across the lower saturated–unsaturated boundary, should perhaps not be neglected. Solute and gas transport (and exchange) from the more confining layer may be particularly relevant in the case that a hydrologically slowed zone underlies this part of the aquitard (as is expected from the gas bubble production of CH_4 ; see subsequent section). Further studies would be required however, to confirm if such transport and exchange processes might be majorly affecting solute input in the underlying aquifer.

Finally, we note that a duplicate sample was taken at 9.25 m (a, b) where the discrepancy in the $^3\text{He}/^4\text{He}$ ratio likely is due to a small offset in sampling depths. The discrepancy arises because each of the 60-cm copper tubes containing fresh sediment samples are subsequently split into three aliquots that are assumed to be at the same approximate depth (see Materials and Methods section). Two aliquots measured from the same 60-cm copper tubes sample can therefore give slightly varying results. Given the nature of the sample measurements, it is not possible to measure the same sample twice.

Given the above observations in the pore space of the sediments overlying the As-contaminated aquifer at Van Phuc, we conclude that the young aquifer likely exists in a semi-confined or semiunconfined state. From this point, the term semiconfined will be applied to indicate either a semiconfined or semiunconfined aquifer. The existence of a semiconfined aquifer supports previous observations on stable isotope data while also satisfying the lithological observations of the overlying heterogeneous aquitard (see Materials and Methods section). It would therefore seem most plausible that water seeps or percolates into the aquifer through preferential flow paths with higher conductivity originating either from overlying ponds, from the Red River itself, or directly from precipitation.

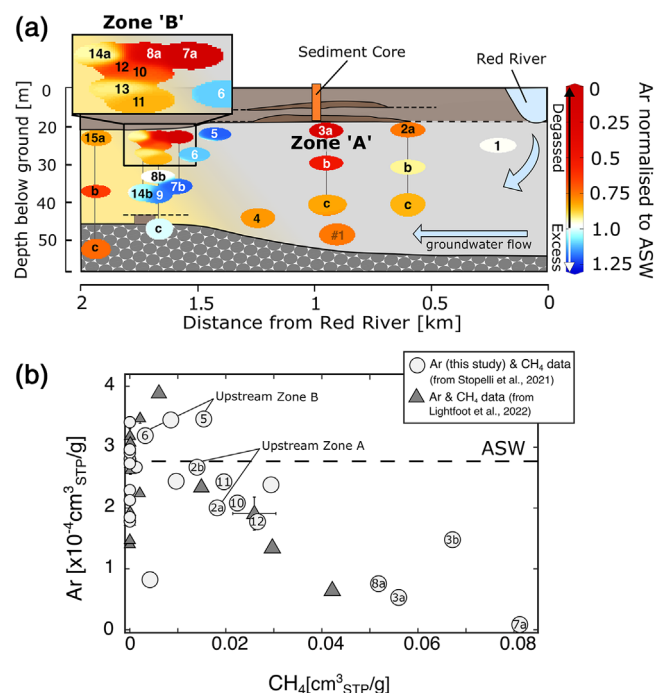


FIGURE 4 (a) Section bathymetry showing the relative excess (blue) and degassing (white-red) of Ar in the groundwater from wells (numbered) situated along the transect (Figure 1). Depths are to the well screens (Supplemental Table S3). Zones A and B show the most strongly degassed groundwater, whereby Zone A coincides with groundwater below the analyzed sediment core (orange rectangle). For exact Ar concentrations and errors see Supplemental Table S3. Standard 1 σ errors for gases analyzed in groundwater samples are <2% for Ne, Ar, Kr, and Xe. 'Degassed' and 'Excess' refer to groundwater degassed and in excess to the expected air saturated water concentrations for this study site (Supplemental Table S1). (b) Ar vs. CH₄ concentrations in groundwater at the study site. Circles show Ar data from wells as taken in copper tubes in our study with corresponding CH₄ data (Supplemental Table S3) from Stopelli et al. (2021). Triangles are data from Lightfoot et al. (2022). Errors are smaller than the data point where not shown. Numbers inside circles correspond to the same well numbers in (a). ASW, air saturated water

3.3 | Groundwater: Widespread degassing linked to in situ CH₄ production

The spatial distribution of Ar concentrations in groundwater along the transect is depicted in Figure 4a, while the decrease in Ar concentrations is observed alongside increasing CH₄ concentrations in Figure 4b. Figures 4a and 4b, show that the most strongly degassed groundwater is present in Zones A and B. Argon data from the newly installed wells and other wells not previously analyzed (Wells 2a–c, 3a–c, 5, 7a, and #3) provides a more comprehensive depiction of Ar concentrations for the transect as a whole, whereas, in our previous paper (Lightfoot et al., 2022), the focus was specifically at Zone B. Importantly, the data set in our study includes noble gas and tritium concentrations in groundwater

directly below the investigated sediment core (Wells 3a and 3b). Analysis from the newly analyzed wells show groundwater is already degassed upstream of Zone B, demonstrating that degassing occurs also in the upstream section of the transect. Notably, several samples (Wells 15a–c, #1, #2, #3) show degassing with no CH₄ present in the groundwater, which can be explained by migration of a degassed water parcel away from a CH₄-producing zone.

The subsurface Ar distribution (Figure 4a) illustrates that groundwater migrating away from the Red River and toward Wells 3a–c becomes increasingly degassed—assuming a directly connected groundwater flow path. If such a flow path continued unhindered, only degassed groundwater downstream of Wells 3a–c should be present. However, Ar concentrations in groundwater downstream of Wells 3a–c show in excess of ASW concentrations (i.e., Wells 5, 6, 7b, 9, and 14b), confirming the presence of an additional non-degassed groundwater flow path intruding the transect either vertically (through preferential flow paths of the overlying sediments) or perpendicularly. This observation of a non-degassed groundwater flow path in the studied aquifer is highly relevant since prior investigations (van Geen et al., 2013; Wallis et al., 2020) have not taken into significant consideration the occurrence of how such interruptions along the transect might affect solute heterogeneity and transport at our study site. The general Ar concentrations surrounding and within Zone B further supports our previous interpretation (Lightfoot et al., 2022), that is, that groundwater by-passes Zone B as a consequence of CH₄ gas bubbles partially obstructing the aquifer pore space. A similar concept of groundwater by-passing the CH₄ producing hotspot at Zone A could therefore also be considered.

3.4 | Influence of aquitard structure on CH₄ formation in the saturated zone

The significant level of degassing coupled with the presence of unsaturated sediments (Figure 2) overlying Well 3a provided motivation to better examine how the overlying stratigraphy influences underlying CH₄ formation in groundwater at the study site. Given the anticipated semiconfined state of the aquifer in conjunction with the observed overlying unsaturated sediments, we conclude that the hydrostatic pressure is lower than previous studies have estimated (Lightfoot et al., 2022; Stopelli et al., 2021). Contrarily, however, it seems unlikely that pressures as low as atmospheric reside at the water table (i.e., zero hydrostatic pressure) as might be assumed for a completely unconfined aquifer.

The following calculation thus redefines the maximum possible in situ saturation threshold of CH₄ at Zone A. The above-cited studies previously assumed a water column of ~12 m above Well 3a in Zone A (as the difference between

an approximated water level at a depth of ~ 8 m [see Stopelli et al., 2021] and well screen at a depth of 20 m). However, given the 4 m of unsaturated pore space observed in our study (Figures 2 and 3), the overlying water column, and therefore also the hydrostatic pressure at a depth of 20 m, should be lowered by at least 30%.

At atmospheric pressure, CH_4 saturates in water at a concentration of 20 mg L^{-1} ($2.9 \times 10^{-2} \text{ cm}^3_{\text{STP}} \text{ g}^{-1}$). The hydrostatic pressure applied assuming a redefined water column of 8 m above Well 3a is approximately 0.78 atm (Supplemental Information). Consequentially, the in-situ saturation concentration of CH_4 is $\sim 37 \text{ mg L}^{-1}$ ($5.2 \times 10^{-2} \text{ cm}^3_{\text{STP}} \text{ g}^{-1}$) and is therefore a respective 15% lower than fully saturated conditions (Stopelli et al., 2021). Applying the same concept to Well 7b (where the most highly degassed sample is observed) results in a 30% decrease in the in-situ saturation concentration of CH_4 compared with fully saturated conditions (e.g., Lightfoot et al., 2022).

Such evaluation, while seemingly trivial, is relevant because the significant extent to which groundwater is observed to be degassed in our study site, would be more consistent with a lower threshold for the in-situ saturation concentration of CH_4 , which, in turn, is particularly sensitive to the anticipated hydrostatic pressure.

Because it was not possible to collect sediments below a depth of 14.25 m (as the increased sand content does not allow for effective sampling of the applied method), information on the depth to which the sediments remain unsaturated is unclear. Groundwater can, however, be sampled at a depth of 20 m. The lower unsaturated layer therefore likely extends down to the water table between 14.5 and 19.5 m. Given the severity of the noble gas depletion observed in Well 3a (Figure 4; Supplemental Table S3), it is tempting to anticipate that some part of the lower unanalyzed sediments between 14.5 and 19.5 m may also be unsaturated, thus reducing the in situ CH_4 saturation concentration threshold further. The above redefined value on the in-situ saturation concentration of CH_4 (37 mg L^{-1}) therefore indicates an upper possible limit, whereas the lower limit (allowing for increased degassing) would be closer to that under atmospheric pressure only (20 mg L^{-1}). Additional details on this calculation can be found in the Supplemental Information.

3.5 | Stability of the CH_4 -producing zones and CH_4 gas release in Van Phuc

Several physical environmental and anthropogenic factors influencing the stability of such high CH_4 -producing zones in the study sites aquifer have already been outlined (e.g., Lightfoot et al., 2022). Such factors include seasonal fluctuations of the water table (Stahl et al., 2016), influences of local pumping (for irrigation), and the potential perforation of such

CH_4 -gas producing zones upon new well installation. Further, the observed regional abstraction of groundwater (Berg et al., 2008; Van Geen et al., 2013), in combination with smaller scale local pumping, can induce transport of porewater and solutes from the more permeable overlying sediments into the aquifer, potentially exacerbating methane producing zones by increasing the input of, for example, organic carbon into the aquifer.

Notably, the degassing in Zone A (Figure 4a) extends to a greater depth than in Zone B. The reason as to why the extent of degassing in Zone B does not reach the same depth as in Zone A could be a consequence of the intruding groundwater just prior to Zone B coupled with enhanced groundwater pumping in the upper aquifer in the direction of Hanoi (see Berg et al., 2008; Stahl et al., 2016; van Geen et al., 2013). In the absence of such a groundwater intrusion prior to Zone A, CH_4 formation in the upper aquifer (at Well 3a) likely additionally influences degassing in the mid-section of the aquifer (at Well 3b). Namely, degassing occurs at Well 3b as a consequence of a reduced hydrostatic pressure induced by the overlying CH_4 bubbles.

Finally, we note that it remains currently unclear as to what happens to the free CH_4 gas, which becomes enriched with both noble and other gases in the groundwater. One possibility is that emanation of CH_4 -rich gas may periodically occur from individual wells, which has been anecdotally observed in a neighboring village (Lightfoot et al., 2022). The CH_4 gas may also encroach and accumulate in the quasi-saturated zone (e.g., Jones et al., 2014).

3.6 | Groundwater samples: Tritium analysis

Figure 5 illustrates tritium (^3H) concentrations from all samples collected in the copper tubes from our study. In general, the younger aquifer is tritium active, while groundwater in the older aquifer is void of tritium, which is in line with previous observations (van Geen et al., 2013; Wallis et al., 2020). Thus, groundwater seems to have more recently recharged into the younger sections of the aquifer. The persistence of degassed groundwater throughout the field site meant that to determine groundwater residence times by tracer gases (e.g., He, ^3H - ^3He dating) was outside the scope of this study given the highly sensitive and often challenging analysis required. Nevertheless, some conclusions can be drawn from the tritium content alone. The highest tritium concentrations in the younger aquifer are observed in Zones A and B (with the exception of Well 7b). We note that Well 12 in Zone B contains equally high tritium concentrations as Well 3a in Zone A (Supplemental Table S3).

Given that the higher tritium concentrations in Zones A and B coincide with particularly high CH_4 , dissolved organic

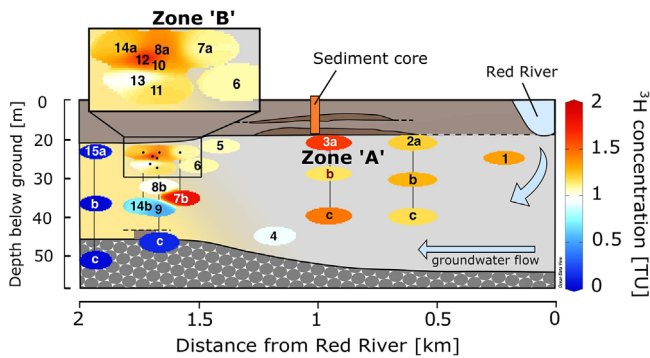


FIGURE 5 Section bathymetry illustrating tritium concentrations in the groundwater of Van Phuc as determined by the ^3H ingrowth method (Clarke et al., 1976). In general, the Holocene groundwater (upstream) is tritium active, while the Pleistocene groundwater is void of tritium. Typical relative errors for ^3H on the analyzed samples are $<15\%$ for $^3\text{H} > 1 \text{ TU}$ and $<30\%$ for $^3\text{H} < 1 \text{ TU}$. Well 14b showed (exceptionally) an error of $\sim 60\%$. Wells 8c and 15a–c were found to be tritium dead, that is, below the detection limit, and have concentrations $<0.06 \text{ TU}$.

carbon, and As concentrations in groundwater also specifically in these two zones (Stopelli et al., 2020, 2021), the interpretation that more recently recharged water percolating along preferential pathways through the heterogeneous upper aquitard and into Zones A and B appears plausible. While the prospect of a younger groundwater component being present is seemingly contradictory within a hydraulically slowed (CH_4 -producing) zone, the manner in which we anticipate groundwater to infiltrate such zones, such as via seepage or slow percolation through preferential pathways in the overlying aquitard, would remain consistent with observations. Further, groundwater (or porewater) moving at a substantially reduced vertical velocity from overlying seepage is more reasonably able to infiltrate underlying gas-forming bubble zones compared with a faster horizontal advective flow. Infiltration of groundwater into the CH_4 -producing zone in this manner would thus provide a solution as to from where the required solutes that sustain such high methanogenic producing zones (and thus As release) is derived.

In the alternate scenario, whereby groundwater in Zones A and B simply represents a higher fraction of post-bomb groundwater, the interpretation generally still supports the overall conceptual model in the higher CH_4 -producing zones: that water renewal is buffered in the CH_4 producing zones, which contain higher residual tritium concentrations from a time when greater amounts of tritium were present in the atmosphere. Notably, however, given the low tritium concentrations and larger errors particularly for samples with between 0 and 1 TU, that is, Wells 4, 9, 8b, and 14b (see Figure 5 caption and Supplemental Table S3), one should be careful not to overinterpret the provided tritium data.

4 | CONCLUSIONS

Our analysis makes the case that to accurately assess the gas dynamics and groundwater transport in aquifers that are subject to high (biogeochemical) gas production, accurate examination, and knowledge of the stratigraphy of the overlying sediments is required. Specifically, we show that partially unsaturated conditions in an overlying heterogeneous aquitard, can (a) be determined through noble gas analysis of the sediment pore space and (b) are a contributing factor in the formation of a free gas phase in the underlying aquifer.

Despite a number of studies recognizing that hydrostatic pressure is a key factor to determine bubble formation in aquifers (Amos et al., 2005; Fortuin & Willemssen, 2005; Mastrocicco et al., 2019), to our knowledge, none have yet considered how such unsaturated pore space in overlying sediments may reduce hydrostatic pressure in semiconfined aquifers and, hence, contribute to in-aquifer gas formation. Such an issue is particularly important in As contaminated aquifers known to have high CH_4 production (Klump et al., 2006; Postma et al., 2012, 2016; Stute et al., 2007) and where contaminant transport and mobilization are necessary to evaluate.

Such unsaturated layers of increased sand content and conductivity may also act as preferential flow paths through which input of solutes may be periodically supplied to groundwater (Gerber et al., 2001; Harrington et al., 2007; Nilsson et al., 2001). Both the excess Ar pattern and tritium results in our study are not in conflict with the prospect that more recently recharged water may percolate along preferential pathways through the upper aquitard and enter the aquifer close to Zones A and B. However, further studies are required to more robustly verify the accumulating evidence implicating groundwater recharge through parts of the aquitard (see also Berg et al., 2008; Eiche et al., 2017; Stopelli et al., 2020, 2021). An increased solute input from the proposed hydraulic connection would, however, rationalize the particularly high As concentrations and continuous CH_4 production in both Zones A and B of the studied aquifer. In addition, $^3\text{He}/^4\text{He}$ and He/Ne ratios results (Figure 3; Supplemental Figure S3) hint that some gas exchange occurs at the saturated and unsaturated interfaces in the investigated sediment core, which could also account for solute input and exchange into the underlying aquifer. Quantification of the specific gas flux at these boundaries was, however, not able to be determined with results from our study.

Although noble gases have previously been applied as tracers through the vadose zone to assess, for example, carbon cycling (Jones et al., 2014) and soil respiration (Freundt et al., 2013), they have not before been applied to identify such hanging pore or groundwater conditions in heterogeneous aquitards. The unique link between noble gases and certain

changes in sedimentological structure of aquitards thus shows their potential to clearly distinguish between saturated and unsaturated layers in heterogeneous sediments.

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AUTHOR CONTRIBUTIONS

Alexandra Kathryn Lightfoot: Conceptualization; Data curation; Formal analysis; Funding acquisition; Investigation; Methodology; Resources; Software; Visualization; Writing – original draft; Writing – review & editing. Emiliano Stopelli: Conceptualization; Data curation; Formal analysis; Validation; Writing – review & editing. Michael Berg: Conceptualization; Formal analysis; Funding acquisition; Supervision; Validation; Visualization; Writing – review & editing. Matthias Brennwald: Conceptualization; Formal analysis; Supervision; Validation; Visualization; Writing – review & editing. Rolf Kipfer: Conceptualization; Formal analysis; Funding acquisition; Investigation; Methodology; Resources; Supervision; Validation; Visualization; Writing – review & editing.

CONFLICT OF INTEREST

The authors report no conflicts of interest.

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SUPPORTING INFORMATION

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