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Noble gas constraints on the fate of arsenic in groundwater

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ABSTRACT

Groundwater contamination of geogenic arsenic (As) remains a global health threat, particularly in south-east Asia. The prominent correlation often observed between high As concentrations and methane (CH_4) stimulated the analysis of the gas dynamics in an As contaminated aquifer, whereby noble and reactive gases were analysed. Results show a progressive depletion of atmospheric gases (Ar, Kr andN_2) alongside highly increasingCH_4, implying that a free gas phase comprised mainly ofCH_4 is formed within the aquifer. In contrast, Helium (He) concentrations are high within theCH_4 (gas) producing zone, suggesting longer (groundwater) residence times.

We hypothesized that the observed free (CH_4) gas phase severely detracts local groundwater (flow) and significantly reduces water renewal within the gas producing zone. Results are in-line with this hypothesis, however, a second hypothesis has been developed, which focuses on the potential transport of He from an adjacent aquitard into the (CH_4) gas producing zone. This second hypothesis was formulated as it resolves the particularly high He concentrations observed, and since external solute input from the overlying heterogeneous aquitard cannot be excluded.

The proposed feedback between the gas phase and hydraulics provides a plausible explanation of the anti-intuitive correlation between high As andCH_4, and the spatially highly patchy distribution of dissolved As concentrations in contaminated aquifers. Furthermore, the increased groundwater residence time would allow for the dissolution of more crystalline As-hosting iron(Fe)-oxide phases in conjunction with the formation of more stable secondary Fe minerals in the hydraulically-slowed (i.e., gas producing) zone; a subject which calls for further investigation.

1. Introduction

Globally, many valuable groundwater resources are severely affected by high levels of arsenic (As) (Naujokas et al., 2013; Nordstrom, 2002; Podgorski and Berg, 2020; Smedley and Kinniburgh, 2002). Particularly in the river-deltaic regions of south and south-east Asia, As contaminated aquifers, which supply water for local drinking and irrigation, coincide with high population densities (Berg et al., 2007; Buschmann et al., 2008; Fendorf et al., 2010), culminating in a high risk of As exposure and detrimental health impacts (Abedin et al., 2002; Berg et al., 2001; Buschmann et al., 2008; Huq et al., 2006).

To understand the origin and extent of As contamination in affected aquifers, the spatial distribution of As (Fendorf et al., 2010; Podgorski and Berg, 2020), how As partitions between aqueous and solid phases, and the biogeochemical mechanisms controlling the partitioning of As, have been topics intensively investigated over the last two decades. A crucial conclusion of these studies, is that As mobilization primarily occurs in conjunction with the microbially mediated reductive

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dissolution of iron-(oxyhydr)oxides (Anawar et al., 2006; Berg et al., 2007; McArthur et al., 2001; Nickson et al., 2000; Ravenscroft et al., 2011), which is often controlled by the availability of suitable organic carbon sources (Wallis et al., 2020). This reductive dissolution mechanism is commonly accompanied by positive correlations of As concentrations with iron (Fe), dissolved organic carbon (DOC), ammonium (NH_4^+) and methane (CH_4) concentrations in groundwater (Dowling et al., 2002; Harvey et al., 2002; Postma et al., 2007; Ravenscroft et al., 2011; Stopelli et al., 2020).

One of the most puzzling observations is the often close correlation between high As andCH_4 concentrations (Dowling et al., 2002; Jessen et al., 2008; Postma et al., 2007). Although such studies suggest thatCH_4 is an indicator of organic matter degradation, no specific mechanism to explain the correlating relationship between As andCH_4 was identified. More recently, however, Glodowska et al. (2020b) found evidence for a potential reaction pathway, in whichCH_4 acts as electron donor for the direct microbially mediated reduction of Fe-oxides and concurrent As release. Yet, a full mechanistic link between As andCH_4 gas production, which also considers hydrogeological processes, remains undetermined. Deciphering such a possible link calls for an in-depth analysis of the overall gas dynamics that characterizes As-bearing, hydrochemically reduced aquifers.

Elucidating the behaviour of the reactive gasCH_4 requires to simultaneously study the evolution of carbon dioxide (CO_2) and nitrogen (N_2), since these gases are also considerable contributors to the total dissolved gas pressure (TDGP) in groundwaters; therefore making them likewise relevant for determining the overall gas dynamics of an aquifer. Importantly, where TDGP exceeds the in-situ hydrostatic pressure of an aquifer, a free gas phase will form due to exsolution of oversaturated gases within the groundwater (Fry et al., 1997). The formation of such free gas phases can locally reduce the hydraulic conductivity and significantly interrupt groundwater flow (Amos and Mayer, 2006; Fortuin and Willemsen, 2005; Fry et al., 1997; Heilweil et al., 2004; Ryan et al., 2000; Thomas et al., 2003). While the observation of a free gas phase existing beneath the water table of As-contaminated aquifers has been previously observed (Postma et al., 2012; Stute et al., 2007), no attempt to link such a change in the physical transport characteristics to As concentrations and distributions within contaminated aquifers has been made to date.

In this study, we hypothesize that such in-aquifer gas phase production can result in vastly increased groundwater residence times, therefore increasing exposure times among critical reactants that govern kinetically controlled As release. In particular, an increased residence time allows for e.g., the reductive dissolution of more crystalline and thus less reactive forms of iron and associated As release, and more stable Fe(II) minerals to form. Thus, studying the production and evolution of reactive gases in (hydrochemically) reduced groundwater is an important aspect, which allows us to elucidate a previously overlooked hydrogeological mechanistic link betweenCH_4 production and elevated As concentrations in affected groundwater flow systems.

By combining noble gas tracer techniques (Kipfer et al., 2002) with the analysis of reactive gas species in groundwater, we employ a unique tool set to determine gas and groundwater dynamics in an As contaminated aquifer. We evaluate our hypothesis for a well-studied aquifer near Hanoi, Vietnam, where complex and interlinked hydrogeological and biogeochemical processes govern the fate of As. We assess how the analysed gases co-evolve, and how they evolve in relation to As groundwater concentrations, with the overall aim to establish a mechanistic link betweenCH_4 gas formation and elevated As concentrations.

2. Materials and methods

2.1. Field site: background and geological setting

The selected study site near Hanoi, Vietnam, has a rich history of detailed investigations that began over two decades ago. The first in-depth study to disclose the extent of As contamination along the alluvial planes of the Red River deltaic region was performed by Berg et al. (2001). These initial findings were complemented by subsequent studies characterizing the geological, lithological, mineralogical, and hydrochemical features of the delta. Many of these studies have paid particular attention to the aquifer system underlying the village of Van Phuc (Berg et al., 2008; Eiche et al., 2008; Glodowska et al., 2020a; 2020b; Kontny et al., 2021; Neidhardt et al., 2021; Nghiem et al., 2020; Stahl et al., 2016; Stopelli et al., 2020; van Geen et al., 2013; Wallis et al., 2020), mostly due to the notably high As concentrations, but also because the observed small-scale spatial variability of As concentrations is highly representative of many other As-affected field sites.

The Van Phuc aquifer system, also the focus of this study, is situated 15 km south-east of Hanoi, inside a meander of the Red River (Fig. 1). The study site was selected since it is well characterized and highly typical for geomorphological deltaic structures comprised of more recent sediment depositions that have repeatedly shown to be associated with high As concentrations (Ravenscroft et al., 2005; Smedley and Kinniburgh, 2002; Sutton et al., 2009). At the study site, As concentrations in groundwaters reach approximately 500 μg/L, therefore exceeding the drinking water limits as recommended by the World Health Organisation (WHO) by a factor of up to 50 (Stopelli et al., 2020). A cross-section of the stratigraphic and other aquifer characteristics are illustrated in Fig. 2. The studied transect, at around 2 km long, stretches from the riverbank in the south-east (SE) of the village, towards the north-west (NW). The aquifer below the SE of the village comprises of younger (Holocene), 'grey'-coloured, reduced sediments associated with high As concentrations (Eiche et al., 2008). In contrast, the aquifer below the NW of the village comprises of older (Pleistocene), more oxidized 'orange'-coloured sediments, in conjunction with low As concentrations.

The interface between these two depositional layers, is characterised by a *transition zone (TZ)*. This *TZ* shows inter-layering features between the two lithological fronts (van Geen et al., 2013) and transitional mineralogical assemblages and redox conditions. This lithological boundary and changing redox conditions, are understood to be the root cause for the sudden drastic change in As concentrations, which drop from 500 μg/L upstream of the *TZ*, to less than 1 μg/L some 30 m downstream of the *TZ* (Stopelli et al., 2020; van Geen et al., 2013). Arsenic migration through the *TZ* was further found to be retarded relative to the horizontal groundwater flow (van Geen et al., 2013), most likely and predominantly as a result of As sorbing to the secondary iron minerals that here prevail, particularly microcrystalline iron-(oxyhydr) oxides (Rathi et al., 2017).

Both Holocene and Pleistocene aquifer sections are underlain by a highly-conductive gravel aquifer (Pleistocene: from a depth of around 50 m below ground level), and overlain by a silty-clay aquitard with a thickness of up to 23 m, i.e, from ground level to aquifer. The gravel aquifer contains low As concentrations at <10μg/L (Stopelli et al., 2020). In the central part of the investigated transect (Figs. 1, 2), the thickness of the overlying aquitard is reduced to around 10 m and underlain by alternating silt, silty fine sands and fine sands down to a depth of around 21 m (Eiche et al., 2017; 2008), therefore increasing the permeability in the lower part of the aquitard. In contrast, at the NW end of the transect, i.e., close to multi-level well 11 in Fig. 1, the aquitard is more homogeneous and extends to a depth of around 23 m. In general, sand lenses and lenses rich in peat and organic matter (OM) are observed to be inter-bedded within the aquitard (Eiche et al., 2017; 2008).

Nowadays, the groundwater flow in the investigated transect is in the direction towards Hanoi, from the Red River. The current hydraulic gradient in-fact opposes the natural conditions of groundwater flow (Berg et al., 2008; Stahl et al., 2016; van Geen et al., 2013; Wallis et al., 2020) as a consequence of the large-scale abstraction of groundwater by the municipal waterworks in Hanoi (Fig. 1, *left*). As a result of the flow reversal, surface water from the Red River started to intrude the

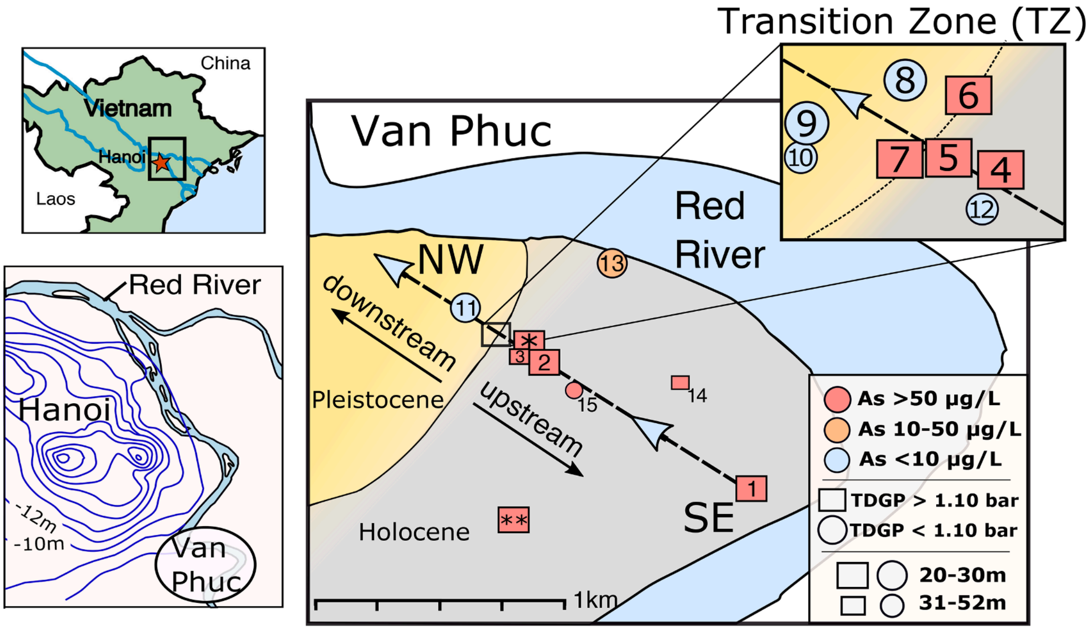

Fig. 1. Aerial schematic of Van Phuc village showing the spatial extent of the underlying aquifers, and a zoom-in of the transition zone (*TZ*). Groundwater flow follows the dashed transect line (i.e. south-east, SE, to north-west, NW; van Geen et al., 2013; Wallis et al., 2020), along which the majority of sampling wells are located. Wells are indicated by numbered circles or squares whereby a larger shape size indicates a shallower well. Squares represent wells with a total dissolved gas pressure (TDGP) >1.1 bar i.e., above atmospheric pressure and correlating with high As concentrations (see Results: Fig. 3, Table 1). Darker (pink) wells have the highest As concentrations. Starred wells (i.e.'*', '**') were wells scheduled for analysis but unsuccessful in obtaining quantitative data. Wells 4 and 11 have multiple depths (see Fig. 2). *Left: Upper & Lower*: Overview of the fieldsite location, 15 km SE of Hanoi alongside the Red River, and including piezometric heads showing the drawdown of groundwater due to excessive pumping from the municipal waterworks, (adapted from Berg et al., 2008).

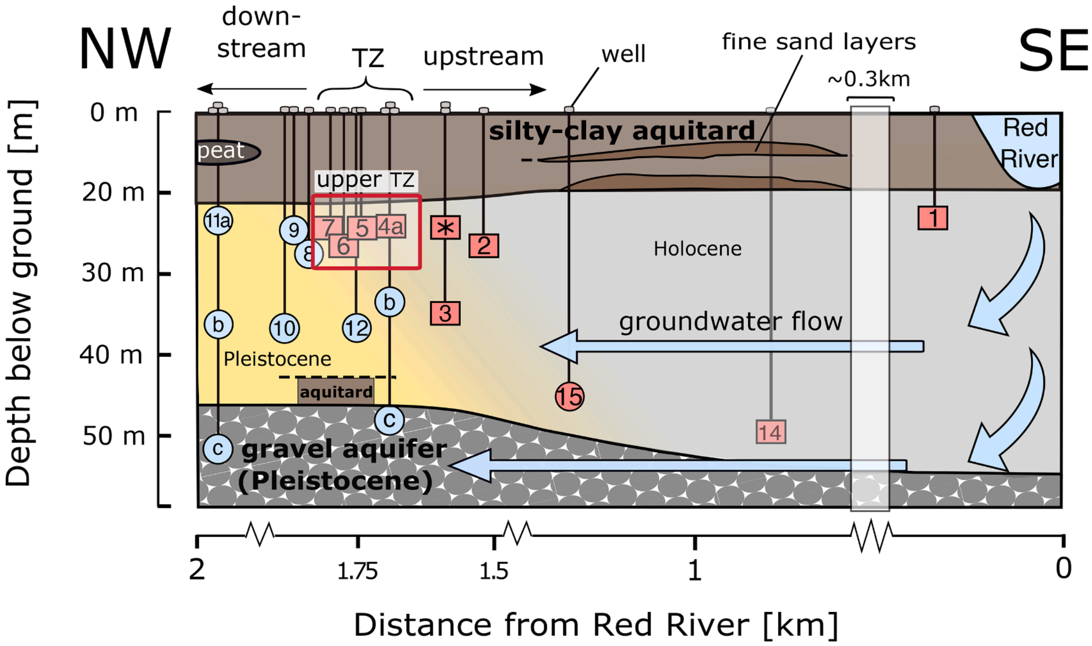

Fig. 2. Schematic of the sub-surface of Van Phuc village following the transect line in Fig. 1. Note the breaks in the x-axis, showing where there is a slight change in the distance range, and indicated since the wells in the transition zone (TZ) are close together when compared to the full extent of the transect. Well 14 is faded since it is not exactly on the transect, but in close proximity. The location of the upper TZ is boxed. Multi-level wells 4 and 11 are sub-categorized into a, b and c, which specify differing depths. For specific well depths and distances from the Red River, see Table 1.

Holocene aquifer from the Red River more than 50 years ago (Stopelli et al., 2020; van Geen et al., 2013), and passed the *TZ* approximately 20 years ago (Wallis et al., 2020). This conceptual hydrogeological model is underpinned by previously measured ^{3}H-^{3}He data (van Geen et al., 2013) and by inverse numerical groundwater flow and transport modelling of these data (Wallis et al., 2020).

While the seasonality of the region varies between dry (November - April) and monsoon (May - October), Stahl et al. (2016) have shown that the Red River replenishes the (Holocene) aquifer year round. This recharging by the Red River is demonstrated by the observation that annual fluctuations of the groundwater table in the (Holocene) aquifer, closely mimic fluctuations of the Red River, but are almost always lower than the Red River by between around 0.3 - 1 m. The recharging of the aquifer from the Red River is further supported by hydrogeochemical data obtained in both seasons (Berg et al., 2008; Stopelli et al., 2020).

2.2. *The role of noble gases*

The gas dynamics of groundwaters can be determined using tracer techniques similar to those applied in studies aimed at groundwater dating and at assessing and quantifying in-situ groundwater mixing processes (Kipfer et al., 2002; Solomon and Aeschbach-Hertig, 2012). For such studies, noble gases are commonly employed as environmental tracers, since they are already present in the groundwater and, importantly, are biogeochemically inert. The non-reactive nature of noble gases allows physical groundwater transport and gas exchange to be separated from chemical reactions, making them particularly useful to elucidate the impact of biogeochemical processes such as denitrification (Blicher-Mathiesen et al., 1998; Popp et al., 2020; Stanley and Jenkins, 2012) or rapid oxygen consumption (Kipfer et al., 2002; Mächler et al., 2012). For detection of a gas phase, noble gases are ideal tracers since they are physically sensitive to partitioning between the liquid and gaseous phases, while remaining insensitive to the biogeochemistry of the surrounding environment (Kipfer et al., 2002; Stanley and Jenkins, 2012). Therefore, analysing the noble gases alongside major reactive gas components in the groundwater are an asset when simultaneously studying biogeochemical gas formation and physical flow and transport processes.

2.2.1. *Sources, sinks and gas dynamics*

To gain a meaningful interpretation of noble gas concentrations in groundwaters, measured gas concentrations are compared with air saturated water (ASW) concentrations of the atmospheric gas species at the typical prevailing conditions for the specific study site (for Van Phuc: T = 25°C, S = 0 g/kg, altitude = 10 masl; see Table 1). Any deviation from expected ASW concentrations allows *excess air* (EA) (Aeschbach-Hertig et al., 2002; Kipfer et al., 2002), *radiogenic* ^{4}He accumulation (Kipfer et al., 2002; Solomon et al., 1996; Strauch, 2014), and *degassing*

Table 1

First row shows air saturated water (ASW) concentrations for He, Ar, Kr, N_2 and CH_4 for the prevailing conditions of the field site. Wells are grouped according to location (Figs. 1, 2) and gas content in the groundwater. Arsenic concentrations are from our publication of Stopelli et al. (2020), where also the details on sampling, analysis and the analytical errors can be found. The error on each gas measurement (i.e., well) is determined as the standard deviation of 3 consecutive measurements, as given in parenthesis following the obtained result and applied to the least significant digit(s) i.e., $3.62(36) = (3.63 \pm 0.36)\ cm^3_{STP}/g$. From Brennwald et al. (2016), the analytical uncertainty for N_2, CH_4 and Ar are <2.5%, for He <3%, and for Kr <4% with the miniRUEDI. GPS co-ordinates of each well can be found in Table 2 in Section S2 of the appendix, alongside CO_2 and O_2 values. Since no specific pattern was observed here for the evolution of CO_2, it not discussed further and results are included only in Section S2 of the appendix for completion of the data set. The unit conversion can here be applied: $1\text{mol} = 22.41 \times 10^3\ cm^3_{STP}$.

Well	Location	Distance from river km ± 1m	Depth to screen m ± 1.5m	He ($\times 10^{-8}$) cm^3_{STP}/g	Ar ($\times 10^{-4}$) cm^3_{STP}/g	Kr ($\times 10^{-8}$) cm^3_{STP}/g	N_2 ($\times 10^{-2}$) cm^3_{STP}/g	CH_4 cm^3_{STP}/g	TDGP bar	As µg/L
ASW	-	1	-	4.41	2.84	6.18	1.11	$< 10^{-12}$	1.01	-
1	upstream	0.25	23	3.62(36)	3.17(12)	6.22(35)	1.82(2)	$2.63(16) \times 10^{-5}$	1.42 (<1)	138
2	upstream	1.50	25	4.28(6)	3.45(8)	7.13(17)	1.61(1)	$2.14(2) \times 10^{-3}$	1.32 (<1)	340
3	upstream	1.64	35	4.75(11)	3.87(3)	7.59(4)	1.45(1)	$6.06(5) \times 10^{-3}$	1.33 (<1)	352
4a	upper TZ	1.74	23	7.43(48)	0.65(5)	1.33(19)	0.14(1)	$4.22(6) \times 10^{-2}$	1.60(2)	387
5	upper TZ	1.75	23	4.76(30)	2.03(25)	4.55(1)	0.66(5)	$2.85(15) \times 10^{-2}$	1.58(7)	271
6	upper TZ	1.75	26	5.24(10)	2.32(3)	6.35(30)	0.77(1)	$1.49(2) \times 10^{-2}$	1.16(1)	51
7	upper TZ	1.76	23	5.49(14)	1.35(3)	3.37(10)	0.34(1)	$2.96(1) \times 10^{-2}$	1.33(1)	74
8	downstream	1.77	23	3.20(11)	2.61(6)	5.57(26)	1.04(1)	$1.25(4) \times 10^{-4}$	0.84 (<1)	2
9	downstream	1.79	22	3.56(51)	2.76(9)	6.71(27)	1.10(1)	$4.45(21) \times 10^{-5}$	0.88 (<1)	1
10	downstream	1.80	36	3.33(9)	2.85(1)	5.98(23)	1.09(1)	$1.05(1) \times 10^{-4}$	0.90 (<1)	<1
11a	downstream	2.00	22	2.96(19)	1.84(3)	4.29(72)	0.77(1)	$4.76(8) \times 10^{-6}$	0.66 (<1)	1
11b	downstream	2.00	36	2.93(7)	1.46(1)	2.92(37)	0.62(1)	$3.98(3) \times 10^{-6}$	0.56 (<1)	<1
11c	downstream	2.00	52	3.85(16)	1.76(1)	3.87(76)	0.85(1)	$4.50(20) \times 10^{-6}$	0.71 (<1)	8
4b	below TZ	1.74	32	3.24(18)	2.71(4)	6.35(10)	1.08(1)	$2.83(24) \times 10^{-5}$	0.87(1)	2
4c	below TZ	1.74	47	4.23(59)	2.84(10)	6.80(63)	1.20(5)	$2.28(6) \times 10^{-5}$	1.02(4)	9
12	below TZ	1.75	36	3.87(6)	3.05(7)	7.11(24)	1.30(1)	$1.06(3) \times 10^{-4}$	1.05(1)	3
13	north of transect	0.10	23	2.75(13)	1.39(1)	2.51(61)	0.55(1)	$6.70(13) \times 10^{-6}$	0.49(1)	22
14	deeper Holocene	0.92	45	2.85(4)	1.92(1)	4.53(14)	1.37(1)	$5.84(1) \times 10^{-5}$	1.13 (<1)	88
15	deeper Holocene	1.27	45	3.17(8)	2.23(2)	4.93(8)	0.90(1)	$2.08(1) \times 10^{-3}$	0.80 (<1)	186

effects to be quantified; all of which are indicative that some physical process has occurred in the studied aquatic environment.

EA is formed in response to a fluctuating water table, and is identified in groundwaters where the full range of atmospheric noble gas concentrations exceed their ASW concentrations. This atmospheric excess arises as the fluctuating water table traps air pockets in the quasi-saturated soil zone, which are subsequently subject to an increased overlying hydrostatic pressure as the water table rises, thus forcing the excess atmospheric gases to dissolve into the groundwater (Aeschbach-Hertig et al., 2000; Kipfer et al., 2002). In addition, ^{4}He accumulates in ground/pore-waters due to the radioactive decay of Uranium (U) and Thorium (Th) naturally abundant in the aquifer (and aquitard) matrix (Kipfer et al., 2002). A large excess of He in groundwater is therefore indicative of radiogenic ^{4}He accumulation, which allows for the qualitative dating of older ground/pore-waters in the range 10^3-10^8 He years (Solomon et al., 1996).

Degassing is the only physical process that produces noble gas concentrations lower than ASW concentrations. Degassing describes the removal of dissolved gas species in the groundwater as a consequence of their re-partitioning between the groundwater and a newly formed gas phase (Aeschbach-Hertig et al., 2008; Brennwald et al., 2005; Visser et al., 2007). Thus, noble gas concentrations below their ASW concentrations are indicative that degassing has occurred. Degassing can be an artifact of sampling, i.e., due to the reduction of the hydrostatic pressure as groundwater flows upward within a monitoring borehole, or can occur in-situ beneath the water table, where biogeochemical gas production has increased the TDGP above the local hydrostatic pressure of the aquifer (Fortuin and Willemsen, 2005; Klump et al., 2006; Mookherji et al., 2003; Stute et al., 2007; Visser et al., 2007). To avoid degassing upon sampling in our field site, an electric submersible pump was used and tight (clamped) connections between the clear tubing and entrance to the membrane module input was ensured (see below for details on analytical set-up). No bubbles entering the module were observed during analysis.

2.3. Sampling and analysis

In November 2018, a field campaign was carried out in which the miniRUEDI (Gasometrix GmbH, Switzerland, see Brennwald, 2018), a self-contained portable mass spectrometer, was installed at 19 pre-existing wells. The miniRUEDI determined noble and reactive gas concentrations in the groundwater (Figs. 1, 2: wells 1–15). Before analysis with the miniRUEDI, each well was purged and observed to stabilize with respect to pH, salinity andO_2 concentrations. For wells marked with a '*' in Figs. 1, 2, quantitative sampling was not possible, as they tended to run dry after a few minutes of pumping. Nevertheless, some qualitative observations from the well with a single '*', provides valuable complimentary information, which have been detailed in the discussion and Section S1.2 of the appendix.

The miniRUEDI continuously quantifies dissolved gas partial pressures in water which traverses through a membrane module. The gas permeable membrane separates-out gases dissolved in the water, into a head-space. The head-space is connected to the mass spectrometer via a 11 m long capillary through which a small fraction of the gas in the head-space is abstracted. In addition, water temperature and TDGP in the head-space are continuously recorded (GE-MIMS-APP, patent pending). Further details on the functionality of this instrument are described in Brennwald et al. (2016).

For the Van Phuc field site, the miniRUEDI was set-up to measure He, Ar, Kr,N_2,O_2,CO_2 andCH_4 partial pressures in groundwater wells. A tailored gas mixture consisting of 1%CH_4, 1%CO_2, 1%H_2 and 97%N_2 was used for calibration ofCH_4 andCO_2, in addition to ambient air as a standard for calibration of the remaining gases (i.e.N_2,O_2, He, Ar, Kr). Partial pressures for the analysed gases can be converted into concentrations ofcm^3_{STP}/g (centimeter cubed of gas at standard temperature (0°C) and pressure (1 atm), per gram of water) by applying Henry's Law (Kipfer et al., 2002; Solomon and Aeschbach-Hertig, 2012). Typical analytical uncertainties for the gas analysis carried out by the miniRUEDI are given in Table 1.

Table 1 further details three key (spatial) zones identified within the field site (Also shown in Figs. 1, 2). Specifically, the 'upper *TZ*' denotes wells situated in the upper part (approximately 20 - 30 m in depth) of the *TZ*. 'Upstream' and 'downstream' zones describe wells situated upstream and downstream, respectively, to the upper *TZ*. Wells which fall outside of these three specified zones are located as described in Table 1. Notably, while some wells 'outside' could in principle be assigned to one of the identified zones, data is also grouped according to dissolved gas and As concentrations, in an effort to gain a meaningful understanding of the overall gas-evolution of the field site.

3. Results and discussion

3.1. Patterns in TDGP,N_2,Ar, Kr andCH_4 data

The measured TDGP values vary considerably between 0.5 and 1.6 bar, with clear variations recognizable among the three previously specified zones. This variation in TDGP, along with corresponding As concentrations, is illustrated in Fig. 3 for all analysed wells. High concentrations of As are found particularly in the wells where the TDGP exceeds 1.1 bar, therefore implying that As exhibits a relationship with the gas specie(s) that contribute to these high TDGPs.

The different zones are similarly identifiable in Fig. 4A and B, in which He,N_2, Ar and Kr concentrations have been plotted as functions ofCH_4 concentrations. Notably, within the upper *TZ* of Fig. 4B, He displays a distinctly different correlation withCH_4 compared to the purely atmospheric gases displayed in Fig. 4A. Since the atmospheric gas concentrations and corresponding trends withCH_4 vary spatially, the gas dynamics in each zone are evaluated and discussed individually before observations are synthesized to an overall conceptual model of the gas dynamics and its controls as well as its impacts.

TDGP highest in the upper TZ

Wells 4a - 7 show some of the highest TDGP values, ranging between 1.2 - 1.6 bar (Table 1, Fig. 3) that correlate strongly with increasing As concentrations. These wells additionally have elevatedCH_4 concentrations, reaching up to$4.2 \times 10^{-2} cm^3_{STP}/g$ (Table 1), therefore linking TDGP toCH_4 production and high As concentrations within the upper *TZ*.

Although TDGP is high in the upper *TZ*, Ar, Kr andN_2 concentrations are depleted with respect to ASW values, whereby this depletion is highly correlated to increasingCH_4 concentrations (Fig. 4A). The observed correlation implies that this gas loss is a result of in-situ degassing in response toCH_4 over-saturation within the aquifer.

In the most extreme case, around 80% of the expected dissolved atmospheric Ar, Kr andN_2 has been lost from the water phase. If, prior to degassing, the groundwater contained EA, the above estimate for gas loss would be higher still. Further details regarding the in-situ saturation threshold ofCH_4 for this specific aquifer, can be found in Section S1.1 of the appendix.

High TDGP and EA upstream of the TZ

Wells 2 and 3, situated around 100 m upstream of the upper *TZ*, show a likewise elevated TDGP to wells in the *TZ*, thoughCH_4 concentrations are an order of magnitude lower (i.e.$10^{-3} cm^3_{STP}/g$). Here, the high TDGP is explained additionally by enhanced concentrations of atmospheric gases (due to EA formation; Ar: 10 - 35%, Kr:$\leq$ 23%, see Fig. 4A) in conjunction with the enhancedCH_4 concentrations. This observed noble gas enrichment suggests that before enoughCH_4 is produced to trigger exsolution near the *TZ*, the groundwater is over-saturated in atmospheric gases as a result of EA formation.

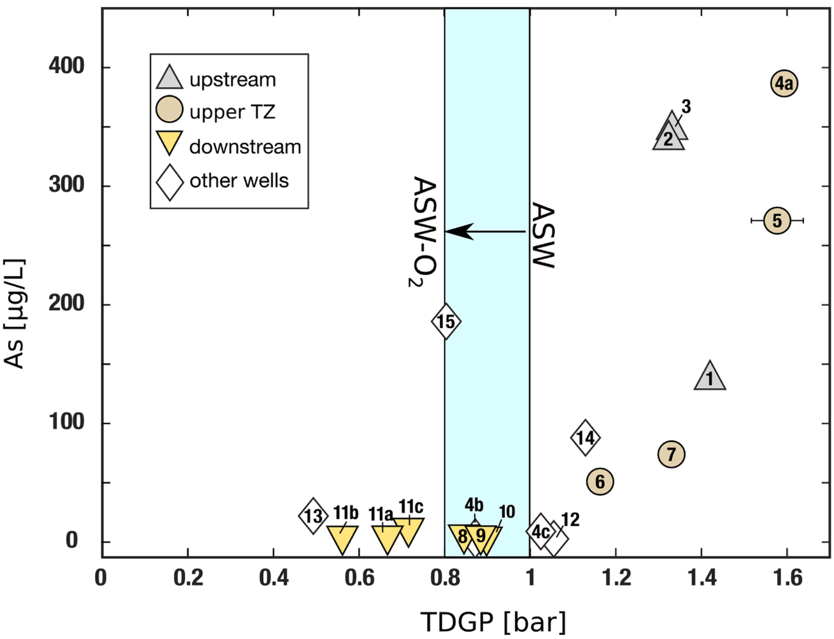

Fig. 3. Arsenic concentrations as a function of total dissolved gas pressure (TDGP) from analysed wells (numbered) at the field site. Wells with the highest TDGP are situated inside the upper *TZ* (olive circles) and upstream (grey triangles), and coincide with the highest CH_4 concentrations (see Table 1; also square wells in Figs. 1, 2). Downstream (inverted yellow triangles), several wells exhibit a TDGP significantly less than 1 bar, confirming severe gas loss. Diamonds (white) are wells not associated with specific zones. For air saturated water (ASW), the TDGP would be expected to agree with the local atmospheric pressure, however, reducing aquifer conditions means O_2 is rapidly consumed (results in Section S2 of the appendix, Table 2), thus decreasing the usual ASW pressure by up to 20%, as illustrated in blue (shaded). In all data points, the error bar for TDGP is smaller than the shape, apart from well 5, which has an error of just over 4%. See Table 1 for individual errors. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

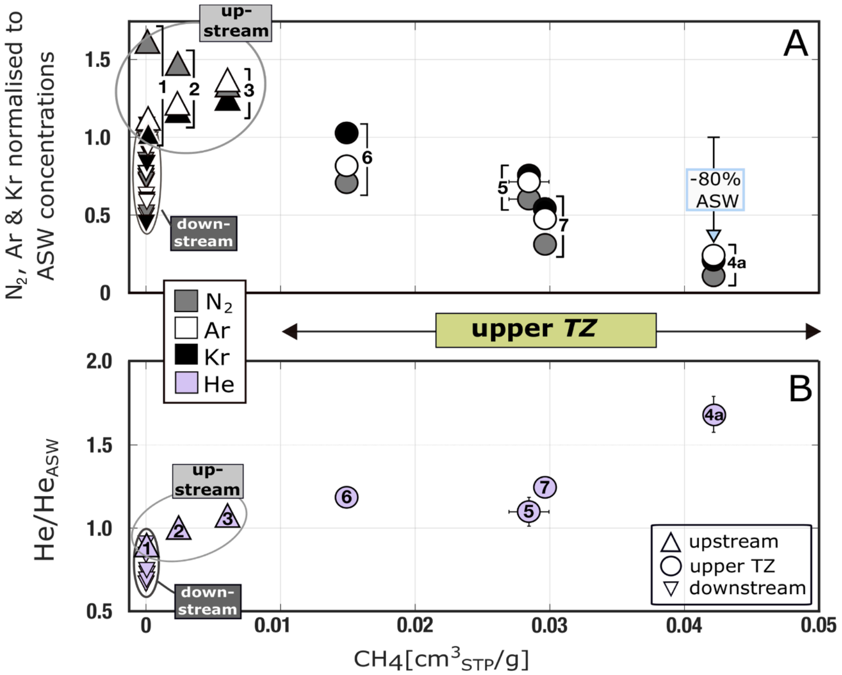

Fig. 4. **A**: N_2 (grey), Ar (white) and Kr (black) continuously decrease as CH_4 concentrations increase in the upper transition zone *(TZ)*, whereas in **B**, He (violet) increases for the corresponding wells. Both **A** and **B** share the same lower x-axis and legend, with all atmospheric gases normalised relative to their ASW concentrations (Table 1). Symbols further clarify the different zones i.e. upstream: upper triangles, upper *TZ*: circles, and downstream: downward triangles. Wells are indicated by the numbers next to data points in **A**, and inside He data points in **B**. For the downstream data points numbering is omitted for clarity, though collectively these data points correspond to wells 8 - 11c. Error bars are omitted where the error is <4%. Data from ‘outside’ of the zones are not plotted in this figure but reviewed accordingly in the text, with the exception of well 15, which is detailed in Section S1.4 of the appendix.

Well 1, situated close to the river (approx. 1.5 km upstream of the *TZ*), follows a similar trend in TDGP and As concentrations to those in the upper *TZ* (Fig. 3). However, in contrast, it has negligibleCH_4 concentrations (Table 1, Fig. 4). ExcessN_2 is instead responsible for the enhanced TDGP of well 1. ThisN_2 excess, at around 60%,seems clearly attributed to denitrification - and is not a result of EA formation, since comparatively, He, Ar and Kr concentrations for this well are either below or close to ASW concentrations (Table 1). Although the upper *TZ* and well 1 similarly contain both high As concentrations and a high TDGP, the two groundwater types are fundamentally (hydrochemically) different: the enhanced TDGP near the river is primarily the result of nitrate reduction, while the TDGP within the more anoxic environment in the upper *TZ* is dominated byCH_4 production.

Downstream zone shows unexpected noble gas concentrations

While the general prevailing hydraulic gradient (van Geen et al., 2013; Wallis et al., 2020) would suggest that the gas depleted groundwater in the upper *TZ* should migrate downstream towards wells 8 - 10, the gas concentrations in these wells are clearly not characteristic of such a flowpath.N_2, Ar and Kr concentrations in wells 8 - 10, are more representative of ‘ASW-like’ groundwater concentrations, subject perhaps only to a very slight gas loss. The TDGP in wells 8 - 10 therefore logically range between 0.8 - 0.9 bar (Fig. 3), since only negligible concentrations ofCH_4 are found. Notably, the atmospheric gas concentrations in wells 8 - 10 are similar to those in wells 4b and 12, situated just below the upper *TZ* (depths 32 m and 36 m respectively, Table 1).

Groundwater strongly affected by degassing

A further 250 m downstream of the upper *TZ*, wells 11a - c show greatly reduced TDGP (0.5 - 0.7 bar, Fig. 3) in conjunction with significantly depleted concentrations of all the atmospheric gases, relative to ASW concentrations (Table 1), although noCH_4. For these wells, we can conclude that the groundwater was, in the past, subject to an in-aquifer degassing process. This interpretation does not limit groundwater here to having passed exactly through the upper *TZ* area - any similarlyCH_4 active (or gas producing) zone in the young aquifer could be responsible for the observed gas loss. Notably, well 13, outside of the transect (Fig. 1, Table 1), shows similar results with a TDGP of only 0.5 bar and excessively depleted dissolved atmospheric gases. Collectively, these results demonstrate that the local groundwater is strongly affected by in-situ degassing.

3.2. Patterns in He data

He accumulation in the upper TZ

In the case of degassing, He, as the most volatile noble gas, is expected to be comparatively more depleted (with respect to ASW) thanN_2, Ar and Kr. However, such a depletion for He is not observed in the upper *TZ*, where He concentrations instead increase with increasingCH_4 concentrations (Fig. 4B). Clearly, the most strongly degassed groundwater well (forN_2, Ar and Kr) in the upper *TZ* coincides with the highest He concentration. Given these stark comparative differences betweenN_2, Ar, Kr and He concentrations, we anticipate an additional non-atmospheric He component (i.e., from radioactive decay and accumulation) is here present. Further, we can surmise that some mechanism exists which produces a positive correlation between the additional He component and the observedCH_4 concentrations.

Approximate residence time in the upper TZ

Qualitatively, the observed He concentrations can be applied to approximately determine the residence time of groundwater within the upper *TZ* (Kipfer et al., 2002; Strauch, 2014). Utilizing concentration data from well 4a, and assuming crudely that all excess, i.e., above ASW, is the result of radioactive production of^{4}He within the aquifer, initial groundwater residence time estimates are calculated to be around 10 ka (see Section S1.5 of the appendix for detailed calculation and discussion).

Reported^{14}C dating results across the transition zone show an increase in deposition age from 11 ka in the grey (Holocene) sediments, to 13 ka in the *TZ*, and 25 ka in the orange (Pleistocene) sediments (see SI of Nghiem et al. (2020), Table S2). Our groundwater age approximation as a result of in-situ radiogenic He accumulation, is therefore in-line with these results, although on the upper limit of what might be reasonably expected.

However, caution must be exercised when interpreting such groundwater estimates as a real age, and we conclude that our estimate of groundwater residence time is at best an order of magnitude approximation. Yet, only such an approximation is here necessary, where the aim is to compare with previously published groundwater ages in the upstream zone. To this point, groundwater in the upstream zone was recharged around 5 - 6 decades ago, according to^{3}H -^{3}He dating (van Geen et al., 2013; Wallis et al., 2020). Thus, the observed non-atmospheric He excess in the upper *TZ* clearly suggests much larger groundwater residence times than those reported upstream.

Typical He concentrations in upstream zone

Wells 2 and 3 show He values close to and slightly above ASW concentrations, respectively. Since He is more sensitive to EA than the heavier noble gases (Kipfer et al., 2002), one would expect the relative (to ASW) EA component to be larger for He than Ar and Kr, in these wells. The opposite, however, is observed in Fig. 4, implying groundwater here was subject to a slight degassing. Since generally, only the typical EA component for He is present in these upstream wells, we conclude that the residence time of the groundwater is short enough to prevent substantial radiogenic ^{4}He from accumulating. Results from these wells are therefore in agreement with available ^{3}H - ^{3}He age data (van Geen et al., 2013; Wallis et al., 2020).

High He concentrations not (significantly) transported outside the upper TZ

Similarly toN_2, Ar and Kr, the He concentrations in the downstream zone, are slightly less than the expected ASW concentrations, and are therefore contrasting with He concentrations in the upper *TZ*. This drastic change in He concentrations between the upper *TZ* and specifically around 30 m downstream, again implies that groundwater from the upper *TZ* is not efficiently transported downstream (wells 8 - 10). Further, He concentrations in these downstream wells are comparable to He concentrations in the wells just below the upper *TZ* (wells 4b, 12; Table 1). Thus, the high He concentrations in the upper *TZ* are also not observed in the few meters below the upper *TZ* (wells 4b, 12).

3.3. Inferred gas dynamics and groundwater evolution

The observed gas patterns in groundwater of the Van Phuc aquifers draw a complex picture of the gas evolution, particularly within and surrounding the upper *TZ*. Notably, gas production, high As concentrations, and high He concentrations prevail in the upper *TZ* area. These observations, in conjunction with the severely contrasting gas concentrations between wells surrounding (wells: 8, 9, 10, 4b, and 12) and wells within the upper *TZ*, support our conceptual model (Hypothesis I), which can explain both the gas and groundwater quality evolution at our study site.

Principally, hypothesis I expands on the already well documented fact that, in aquatic systems where the (e.g., microbiological) production of gases is significant enough to generate in-situ a free gas phase (i.e., gas bubbles), the formed gas phase subsequently blocks part of the available aquifer pore space thus reducing the hydraulic conductivity (Amos and Mayer, 2006; Fortuin and Willemsen, 2005; Fry et al., 1997; Heilweil et al., 2004; Ryan et al., 2000). Applying this concept to the vicinity of the upper *TZ* signifies thatCH_4, as the dominating gas species, oversaturates and stimulates not only the degassing of the atmospheric gas species in the groundwater, but also constrains groundwater flow through and out of the (CH_4) gas producing zone (Fig. 5).

Hypothesis I thus unifies several key observations in our data, i.e., that (1) a reduced hydraulic conductivity in the upper *TZ* vicinity explains why the concentrations of He, Ar, Kr, andN_2 are so dissimilar between the upper *TZ* and the surrounding wells - namely because only the upper *TZ* wells are subject to reduced groundwater flow and continuous degassing; (2) it rationalizes the observed correlation between He andCH_4 - but also the correlation between the excessively degassed atmospheric gas species andCH_4 (Fig. 4); and (3), it explains the discrepancy in groundwater residence times between the upstream zone and upper *TZ* i.e., since the accumulation of (non-atmospheric) He is directly related to the residence time.

Given our observations and the distribution of dissolved gases within the studied aquifer, we envision that when gas bubbles ofCH_4 form in the vicinity of the upper *TZ*, groundwater from upstream diverts both laterally and vertically i.e. by-passing around the local gas producing zone (Fig. 5). This interpretation is also supported by our finding that the surrounding wells generally, give similar gas concentrations. While the above made points, show that hypothesis I explains the majority of our data set rather well, the high estimation for groundwater residence time in the upper *TZ*, may point to an alternative conceptual model.

This alternative model (Hypothesis II) tags the vertical transport of old He-rich porewater from the upper aquitard into the underlying aquifer (Fig. 5). As previously discussed, some sections of the upper aquitard are more hydraulically transmissive (Eiche et al., 2017; 2008) (see Methods), and therefore may allow porewater and associated solutes to percolate or diffusely migrate into the underlying aquifer. Since aquitard porewaters renew rather slowly, they can accumulate

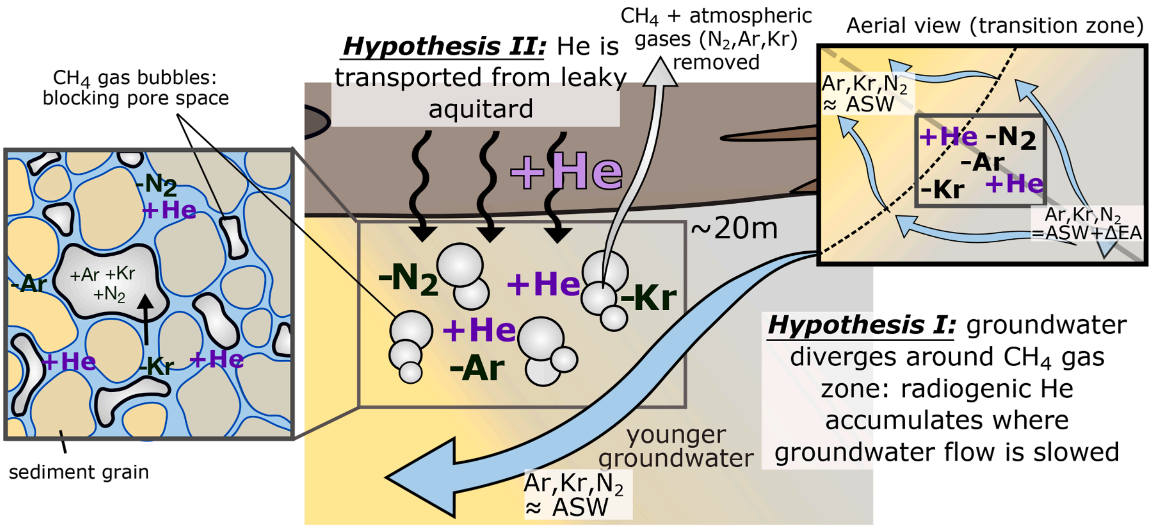

Fig. 5. Gases marked with a ‘ + ’ indicate where gas concentrations are much larger than typical air saturated water (ASW) concentrations, whereas those with ‘ − ’, indicate concentrations significantly lower than ASW (i.e., degassing, see Fig. 4). ***Hypothesis I***: Lateral and vertical deviation of (younger) groundwater flow around CH_4 gas bubbles, which partially blocks the sediment pore space. Hydraulic conductivity is reduced in the bubble producing zone, granting enough time for the non-atmospheric He component to accumulate. ***Hypothesis II***: He is transported into the upper *TZ* from a leaky aquitard and rationalizing the positive correlation between CH_4 and He concentrations in the upper *TZ* (Fig. 4B). In the small (aerial) inset on the upper right, EA = excess air, to which we refer the reader to Section 2.2.1 for specific details.

significant amounts of radiogenic ^{4}He. Thus, input of ^{4}He-rich porewater from the more transmissive sections of the overlying aquitard into the upper aquifer, may also explain the observed He enrichment in the groundwater of the upper *TZ*. The porewaters of such peat-rich layers would likewise be enriched in OM, rationalizing the positive correlation between the concentrations ofCH_4 and He - since the OM supply would fuel the microbially mediatedCH_4 production below the aquitard. This second conceptual model thus provides an explanation for the estimated groundwater age being on the upper limit of what might be reasonably expected, i.e., due to increased input of non-atmospheric He into the upper aquifer.

However, it is important to note that while Hypothesis II provides an explanation for the required OM, and is consistent with the observed correlation between He andCH_4 concentrations, it does not offer an explanation as to why concentrations within and surrounding the wells of the upper *TZ* are so contrastingly different, particularly for the conservative noble gases. Thus, even if this second hypothesis is correct, it cannot alone explain the evolution of gases throughout and surrounding the upper *TZ*. Both hypotheses, however, may simultaneously be valid. Further investigation into the solute and gas composition of the aquitard sediments may allow to experimentally assess the plausibility of this second hypothesis. Particularly, quantification of He concentrations in the aquitard pore water would help to disentangle between the two presented hypothesis.

While degassing in response toCH_4 gas production directly impacts those wells within the upper *TZ* (particularly well 4a), the highest concentrations ofCH_4 for this field-site, are actually observed in well ‘*’, at 58 mg/L (Stopelli et al. (2021); or$8.1 \times 10^{-2} cm^3_{STP}/g$) which has the same depth as well 4a (further discussed in Section S1.2 of the appendix). This implies that the gas producing zone extends further upstream of the *TZ*, where wells 2 and 3 define a boundary in which more ‘normal’ noble gas concentrations in groundwater are observed. Thus, we anticipate that the most favourable conditions necessary for degassing to prevail are specifically between the here defined *TZ* wells and well ‘*’. In principle, however, two independent gas producing hotspots may also exist.

Though the overall observations provide convincing evidence that gas loss as a consequence of in-situ degassing has and may persist to occur within the aquifer, the fate of theCH_4 gas bubbles, which become enriched with both noble and other gases in the groundwater, remains currently unclear. One possibility is that emanation ofCH_4 - rich gas may from time to time occur from individual wells (see discussion in Section S1.1 of the appendix).

3.4. Seasonal and potential anthropogenic influences

One factor yet to be considered, are the effects of seasonal fluctuations in the water table. Annual fluctuations of up to 3 m have been observed in the Holocene aquifer at Van Phuc (Stahl et al., 2016), thus indicating that degassing has the potential to be intensified when the water table drops to its lowest point (around March). As the water table drops, both the hydrostatic pressure and the saturation concentration ofCH_4 is lowered, thus making bubble formation at a specific depth in the aquifer more viable. It could therefore be interesting to repeat a study of the gas dynamics around March time, to confirm how the gas analysis develops into the dry season.

Similarly, increased localised pumping could also exacerbate the production ofCH_4 gas in response to a lowered water table. While there is no current available data on the extent to which groundwater is being pumped to irrigate locally, the overall effect on the here presented hypotheses at the time of the study seems minimal: if local pumping was severe, the forced renewal of groundwater i.e., from underneath the pumped well, would remove the capacity of the hydraulically isolated zone to contain such a large excess in (radiogenic) He, as observed in the upper *TZ*. Notably, however, if the wells are indeed sometimes used for irrigation, some of theCH_4 gas (enriched with atmospheric gases) may be liberated each time the well is opened, thus offering an explanation as to how some of theCH_4 gas may leave the aquifer system.

Conversely, groundwater entrapped in such gas producing zones, may from time to time be released e.g., if the water table significantly rises (increasing the solubility ofCH_4), or, a new well is installed (temporarily releasing gas pressure). We highlight this possibility due to the observation that several wells (i.e., 11a-c, 13 and 15) in the study site, show depletion of the atmospheric gases in conjunction with lowCH_4 concentrations and a TDGP considerably lower than 1 bar - indicating groundwater in those wells must at some point have escaped or bypassed a gas producing zone.

Whilst some of the above discussed seasonal and anthropogenic influences are more speculative than others, it's important to emphasize the sensitivity in the dynamics of such gas producing zones, and consider what consequences such influences may have.

3.5. *Mineralogical observations*

A reduced hydraulic conductivity in aCH_4 gas producing zone, is expected to have an impact on local mineralogy to which As (im) mobilisation is unequivocally linked. More stable Fe(II) minerals and/or a more complete reduction of Fe(III) minerals should in principle form under the precursor of longer groundwater residence times. To properly compare the mineralogy both within and 'outside' a hydraulically-slowed zone, samples from both locations should be acquired, and ideally without the added complexity of a geochemically active redox front nearby. While such comparative data is not explicitly available, some mineralogical observations from sediment cores obtained (at this study site) either adjacent to, or in an alternately predicted gas producing zone, are considered below (Eiche et al., 2008; Kontny et al., 2021; Nghiem et al., 2020).

Distinctively, two independent studies (Eiche et al., 2008; Nghiem et al., 2020), identified the presence of the stable secondary Fe carbonate mineral, siderite, in parts of the younger aquifer where the highestCH_4 concentrations have also been observed. Siderite was specifically observed in sediments close to well '*' (Nghiem et al., 2020; see 'cluster 4' analysis), but also in sediments located more centrally along the transect (Eiche et al., 2008 - whereCH_4 concentrations reach 40 mg/L Stopelli et al., 2021). The point to which siderite is an important observation, is the particularly slow reaction kinetics required for this mineral to form (Postma, 1982). Thus, a hydraulically restricted zone could offer the ideal environment to conceptualize siderite formation. In addition, we note the formation of the secondary Fe-mineral magnetite in the grey sands (between depths of 20 - 30 m) reported close to the upper *TZ*, and implying high rates of Fe(III) reduction (Kontny et al., 2021).

Thus, the mineralogical research so far published (in Van Phuc), are not in contradiction, and in some cases rather corroborate, our conceptual model (namely, hypothesis I). However, given the complexity of the *TZ* mineralogy, caution is required not to over-interpret such data, particularly in the study by Nghiem et al. (2020), where the (cluster) analysis also included some samples from outside the here identified high (CH_4) gas producing zone. For a proper understanding of the mineralogy in a hydraulically-slowed zone, samples should ideally be taken away from the complication of an immediately impinging redox front. Such an analysis, therefore calls for further investigation.

3.6. *Potential consequences on as transport*

The discussed gas evolution and its hydrogeological consequences unquestionably have a profound affect on As transport and distribution in Van Phuc. While our results show that As is itself linked to gas production - in particularCH_4 - the physical effect that such a free gas phase subsequently has on the surrounding environment is an important constraint for predicting future contaminant transport.

In Van Phuc, the riverbed has been previously identified as a key contributor to the source of dissolved As (Wallis et al., 2020). Therefore, As carried downstream towards (localised) gas producing zones, is forced to by-pass around such zones, thus altering the expected As distribution to what might be expected from the current hydrogeological understanding of the field site.

Further, a reduced hydraulic conductivity within an As mobilizing and (CH_4) gas producing hotspot, means the timescales of associated biogeochemical reactions will be substantially affected. As a result of the increased groundwater residence time, more crystalline and hence less reactive forms of iron often linked with As release can be reductively dissolved, while the formation of more stable Fe minerals, as discussed in Section 3.5 is also anticipated.

Accumulation of mobilised As in the (CH_4) gas producing zone, analogously to how He concentrations accumulate here in the upper *TZ*, would also be exacerbated. This point in particular tempts us to formulate a provoking hypothesis based on the general observation of high free gas production and high As concentrations: accumulation of As simply occurs in zones where there is reduced groundwater movement as the (CH_4) gas bubbles do not allow the As to escape. Thus, As accumulates to high concentrations where there is excessive gas (e.g.,CH_4) production, due to a lack of physical transport.

Given the above discussed repercussions that high gas production has on As transport and mobilization, we conclude that such gas producing zones contribute to the wide-spread heterogeneity often observed in contaminated aquifers (Smedley and Kinniburgh, 2002; van Geen et al., 2006).

4. Conclusions

In this paper, we demonstrate that elevated As concentrations could be the consequence of the substantially increased total dissolved gas pressure (TDGP) that is generated by the in-situ biogeochemical production ofCH_4. While degassing (Stute et al., 2007) and elevated TDGP (Postma et al., 2012) have been reported in several contaminated aquifers which exhibit correlatingCH_4 and As concentrations (Dowling et al., 2002; Jessen et al., 2008; Postma et al., 2007; 2012; Stute et al., 2007), the consequence of such gas production in relation to the hydrogeology, mobilization and heterogeneity of As in contaminated aquifers, has until now, not been considered.

We further point out that, while groundwater age generally provides good initial boundary conditions for the hydrogeology of such field sites, assessing groundwater residence times by applying transient trace gas measurements (e.g., ^3H - ^3He) in cases where degassing occurs, is notoriously difficult. As such, alternative methods that give insight to the hydrogeology of contaminated aquifers, becomes hugely beneficial. The combined analysis of reactive gases alongside conservative noble gases in the field, can therefore help not to only reveal in-aquifer degassing events in contaminated aquifers, but also to provide certain constraints on the hydrogeology and thus highlight the relevant timescales necessary to consider for the As mobilizing mechanism itself.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary material

Supplementary material associated with this article can be found, in the online version, at 10.1016/j.watres.2022.118199 .

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