SI Appendix

S1 Supporting observations and calculations

Already in the pilot campaign of autumn 2017, the miniRUEDI determined the TDGP in all groundwater wells at the field site. These first findings showed that wells located within the upper *TZ* had a substantially greater TDGP than the summed partial pressures of all aforementioned gas species. The prevailing biogeochemical conditions in the upper *TZ*, implied that CH_4 was the missing (and dominating) gas component which was not determined by the applied analytical protocol of the 2017 pilot campaign. As a consequence, the 2018 campaign was optimized for CH_4 quantification by equipping the miniRUEDI with an adequate CH_4 calibration gas, with the motivation to quantify the 'missing' gas component. In effect, Hypothesis I was developed from these initial observations.

S1.1 In-situ saturation concentration of CH_4 in the upper *TZ*

To determine if formation of a free gas phase comprising of CH_4 (i.e. bubbles) is physically plausible in the vicinity of the upper *TZ*, the approximate in-situ saturation concentration for CH_4 was calculated. At ambient physical conditions the in-situ saturation value for CH_4 is around 7.2×10^{-2} cm^3_{STP}/g. Here, the hydrostatic (P_{hyd}) + atmospheric (P_{atm}) pressure, i.e. total in-situ pressure, is around 2.47 bar in the respective wells, in which equation:

$$P_{hyd} = \rho g h \tag{1}$$

as been applied. In equation (1): ρ is the density of water, $997\,kg/m^3$; g is the acceleration due to gravity, $9.8\,m/s^2$; and h is the height of the water column, $\sim15\,m$, as the difference between the groundwater table at a depth of $8\,m$, and the well screen at a depth of $23\,m$. An ambient temperature of $25°C$ and a salinity of $0\,g/kg$ were applied to determine the final

₈₀₈ in-situ saturation concentration.

₈₀₉ Whilst acknowledging this value is slightly higher than the measured CH_4 concentrations
₈₁₀ from our data set, agreement is within a factor less than 2. It is important to recognise
₈₁₁ that while measurements are bound to physical well locations, the exact location for the
₈₁₂ highest CH_4 concentration does not hold this restriction. Given the substantial widespread
₈₁₃ gas loss in the groundwater, particularly from wells in the upper *TZ*, it is anticipated that
₈₁₄ such favourable conditions necessary for degassing to prevail are in the nearby vicinity of the
₈₁₅ upper *TZ* wells (most likely in the upstream direction). However, the upper *TZ* area may
₈₁₆ not be the only location where degassing occurs in this field site. Further, P_{hyd} calculated
₈₁₇ above in-fact yields an upper limit for the total pressure, since observations from a nearby
₈₁₈ sediment core (see S1.3) give evidence to suggest that P_{hyd} is substantially lower than here
₈₁₉ assumed.

₈₂₀ Further supporting this argument for an existing free gas phase, is data from Stopelli
₈₂₁ et al. (2021) in which CH_4 concentrations of up to $58\,\mathrm{mg/L}$ (8.1×10^{-2} $\mathrm{cm^3_{STP}/g}$; i.e. TDGP
₈₂₂ $> P_{\mathrm{hyd}} + P_{\mathrm{atm}}$) have been observed in well '✳'. Anecdotal evidence from the neighbouring
₈₂₃ villages to the field site, have also reported that sometimes rather violent emanation of CH_4
₈₂₄ - rich gas from individual (groundwater) wells can occur (B. Bostick, personal communica-
₈₂₅ tion, October 15th 2018, AdvectAs project meeting). These evidences, lead us to conclude
₈₂₆ that it is likely, CH_4 currently over-saturates in (biogeochemically active) parts of the upper,
₈₂₇ young aquifer (and not only in the upper *TZ*), which subsequently leads to the observed
₈₂₈ widespread depletion of dissolved atmospheric gases in the groundwater.

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₈₃₀ S1.2   Observations from well '✳'

₈₃₁ Well '✳', presented great difficulties when attempting to analyze groundwater with the
₈₃₂ miniRUEDI, as it had a tendency to run dry after a few minutes of pumping. Proper gas

measurements with the miniRUEDI were therefore problematic to obtain, however, some interesting observations in the gas data from this well are here important to recognise.

Approximate gas concentrations in well '✻', were roughly similar (in terms of order of magnitude) to those of well 4a in the upper *TZ*, for all gas species (see Table 1). While from Stopelli et al. (2021), it is known that CH_4 concentrations in well '✻' reach 8.1×10^{-2} cm^3_{STP}/g, i.e. above in-situ saturation concentrations. Since well '✻' also contains the highest measured concentrations of As at our field site of $500\,\mu g/L$, noting that CH_4, As, He and TDGP are also potentially very high in this well, provides support to our interpretation (sections 3.3 and 3.6) of the co-evolution of gases and As throughout the aquifers.

S1.3   Overlying aquitard pore water observations

The ongoing preparation of pore water samples from a sediment core taken through the heterogeneous part of the aquitard, located centrally in the transect, has provided important initial observations which add support to our final conclusions that groundwater in Van Phuc is, in general, strongly affected by degassing. The initial step in which pore water is separated from the sediment samples via centrifugation (see Tomonaga et al. (2011)), revealed that a large part of the pore space in that sediment core is not saturated with water, and instead filled with air/gas. The pore space is shown to be unsaturated in two separate layers within the core (between depths of 7.5 - 15 m), indicating the presence of perched groundwater.

These first findings show that the hydrostatic pressure here is lower than the (above) given estimates i.e., since the pore space is not completely occupied by water. Therefore, underlying in-situ production of CH_4, is more likely to result in the formation of a free gas phase. Further analysis of this sediment core, we believe, will lead to an improved understanding on the mechanistic drivers in the degassing process. U and Th concentrations from this sediment core have been additionally applied in the calculation for the groundwater

residence time (see section S1.5).

S1.4   Observations from well 15

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⁸⁶⁰ Well 15 (situated in the deeper section of the upstream zone at 45 m), while it generally

⁸⁶¹ seems an outlier to the more general gas distributions described in this paper, could offer

⁸⁶² an interpretation which would still fit accordingly with the observed gas data this field site.

⁸⁶³ Well 15 contains high As and degassed atmospheric gas species, however shows lower CH_4

⁸⁶⁴ concentrations and very low TDGP, i.e. high As in degassed groundwater. Dissolved gas

⁸⁶⁵ concentrations measured in this well could be explained purely by transport of As away from

⁸⁶⁶ an As mobilization ($+$ CH_4 producing) hotspot. We therefore propose that As *mobilization*

⁸⁶⁷ occurs at such biogeochemically reactive hotspots (e.g. in-situ, upper aquifer) concurrent

⁸⁶⁸ with CH_4 production; whereas As *transport* has occurred where there is degassed groundwa-

⁸⁶⁹ ter coupled with high As concentrations. The degassed groundwater and As are here more

⁸⁷⁰ subject to advective transport, while the free gas phase escapes at the mobilizing hotspot.

⁸⁷¹ This proposition is therefore in-line with the main finding of reactive-transport modelling in

⁸⁷² Wallis et al. (2020), which suggests that after As mobilization at river bed-aquifer interface,

⁸⁷³ advective transport is a major control of As occurrence in the wider area extending from the

⁸⁷⁴ Red River through the young (Holocene) aquifer towards the *TZ*.

S1.5   Estimation of groundwater residence time in the upper *TZ*

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⁸⁷⁶ The following estimate assumes the non-degassed observed He excess is of radiogenic origin,

⁸⁷⁷ is produced only within the aquifer (i.e., in-situ accumulation), and applies the equation

⁸⁷⁸ (Kipfer et al., 2002; Strauch, 2014):

$$\text{groundwater age (yr)} = {}^{4}\text{He}_{\text{rad}}/\text{p}, \tag{2}$$

879 where p = the accumulation rate of the radiogenic ^{4}He, i.e. ^{4}He$_\text{rad}$. Where:

$$p = \rho_{rock}(1 - \phi)/\phi \cdot 0.2355 \times 10^{-12} \cdot ([U] \cdot (1 + 0.123 \cdot ([Th]/[U] - 4))). \tag{3}$$

880 In equation (3) (Kipfer et al., 2002; Strauch, 2014), reasonable estimates for the porosity

881 ($\phi \sim 0.4$ for sandy aquifers (Earle, 2018)), density ($\rho_{rock} \sim 2600[\text{kg/m}^3]$ (Turekian and

882 Wedepohl, 1961; Taylor and McLennan, 1985)), and Uranium ([U] 2.6 ppm) and Thorium

883 ([Th] 11.4 ppm) concentrations (unpublished data) from a sediment core in the central part

884 of the transect of our field site, have been applied. Specifically for well 4a of the field site,

885 this leads to a residence time of just over 10 ka.

886   It is obvious that this estimate is rather crude when considering the complexity of the gas

887 data and it can therefore at best be quantified on an order of magnitude scaling. Depending

888 on the moment (i.e. time) of degassing along the groundwater flow path, an upper and lower

889 limit exists on the amount of ^{4}He$_\text{rad}$ that can be accumulated - which translates to an upper

890 and lower limit on the estimated residence time. The two limits are time sensitive and are

891 often defined by a single degassing event either: (1) before substantial ^{4}He$_\text{rad}$ accumulation,

892 or (2) after significant ^{4}He$_\text{rad}$ accumulation. In (1), very little ^{4}He$_\text{rad}$ is lost in the degassing

893 event, while in (2) almost all of the accumulated ^{4}He$_\text{rad}$ has been degassed. However, in both

894 cases, the ASW component for He will be degassed.

895   Defining these two scenarios as boundaries allows some estimate of an initial upper and

896 lower limit to be set for the groundwater residence time. In the case for well 4a of this field

897 site, the lower limit (1), is already as described, at around 10 ka, whereas the upper limit, (2),

898 gives a considerably larger residence time in the order of 100 ka (to determine the amount

899 of ^{4}He$_\text{rad}$ lost in case (2), we assume a similar amount of degassing for He occurred, as for

900 Ar and Kr i.e. around 80% - see Fig. 4), which is clearly much larger than anticipated.

901   Further complicating the calculation for groundwater residence time is the EA compo-

nent. If some part of the excess He is a result of EA formation, this decreases both the upper and lower limits on the groundwater residence time. Varying the EA component to be between 10% and 70% of the observed excess in well 4a, for example, results in a $^4He_{rad}$ component leading to residence times on a millennial scale i.e. above 1 ka.

Finally, $^4He_{rad}$ residences times as calculated from equation 3, are also largely dependant on the bulk density and porosity of the aquifer matrix, for which here reasonable estimates have been applied. If we similarly vary such parameters within reasonable limits for the studied aquifer, ages within the millennial range are again yielded.

In conclusion, for estimates in the upper residence time range i.e. 100 ka, and therefore degassing according to (2), it would be reasonable to suggest that hypothesis II plays some larger role, whereby diffusive input of He from the overlying aquitard is reflected in the larger groundwater residence times. However, in both scenarios (1) and (2), strong support for Hypothesis I is provided by the substantial excess of He accumulating in the upper TZ, in conjunction with the other previously discussed observations for wells within and surrounding the upper TZ.

S2 Results: Further measurements

Table 2: Additional gases measured by the miniRUEDI alongside the original (local) well names and corresponding GPS co-ordinates of each well. O_2 is strongly depleted relative to its ASW ($\sim 6 \times 10^{-3}$ cm^3_{STP}/g) concentrations for all wells, although in the upper *TZ*, concentrations are an order of magnitude lower due to the highly reducing environment. For CO_2, only partial pressures are here quoted, since the final CO_2 concentrations would depend additionally on the chemical conditions of the water, which were not accounted for in this analysis. The error on each data point (i.e. well) is given here in parenthesis on the according digit.

Original well name	Simplified well name	Location ('zone')	Latitude N	Longitude E	Depth m ±1.5m	O_2 ($\times 10^{-4}$) cm^3_{STP}/g	CO_2 ($\times 10^{-1}$) bar
AMS12	1	upstream	20°54'50.9"	105°54'21.0"	23	6(4).02	0.50(6)
VPNS3	2	upstream	20°55'14.9"	105°53'46.1"	25	0.34(8)	0.72(1)
VPNS5	3	upstream	20°55'17.3"	105°53'41.8"	35	0.27(4)	0.53(1)
AMS11-25	4a	upper TZ	20°55'18.4"	105°53'38.3"	23	0.22(3)	0.47(15)
AMS31	5	upper TZ	20°55'18.5"	105°53'38.2"	23	0.21(6)	0.41(40)
PC43	6	upper TZ	20°55'18.7"	105°53'38.2"	26	0.57(2)	0.40(2)
AMS32	7	upper TZ	20°55'18.9"	105°53'37.6"	23	0.18(1)	0.29(3)
AMS36	8	downstream	20°55'19.6"	105°53'37.6"	23	4.78(10)	0.35(1)
AMS4	9	downstream	20°55'19.38"	105°53'36.17"	22	4.02(8)	0.40(1)
VPNS4	10	downstream	20°55'18.9"	105°53'36.7"	36	3.82(3)	0.56(1)
VPMLA-22	11a	downstream	20°55'23.7"	105°53'31.1"	22	11(2).70	2.49(16)
VPMLA-38	11b	downstream	20°55'23.7"	105°53'31.1"	36	12.84(11)	0.18(1)
VPMLA-54	11c	downstream	20°55'23.7"	105°53'31.1"	52	8.46(83)	0.27(2)
AMS11-32	4b	below TZ	20°55'18.4"	105°53'38.3"	32	4.18(3)	0.41(1)
AMS11-47	4c	below TZ	20°55'18.4"	105°53'38.3"	47	2.64(9)	1.32(4)
PC44	12	below TZ	20°55'18.5"	105°53'38.2"	36	1.54(1)	0.80(3)
AMS15	13	north of transect	20°55'35.8"	105°53'51.7"	23	1.69(2)	0.03(1)
Household #1	14	deeper Holocene	20°55'08.3"	105°54'07.6"	45	1.01(3)	1.17(2)
Household #2	15	deeper Holocene	20°55'08.6"	105°53'50.7"	45	5.14(3)	0.34(1)