

Origin and availability of organic matter leading to arsenic mobilisation in aquifers of the Red River Delta, Vietnam

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Abstract

Groundwater arsenic (As) concentrations in the Red River Delta (Vietnam) are often patchy and related to the microbially induced reduction of Fe oxy-hydroxides. In this study, we explored the influence of the origin, composition and availability of natural organic matter on the hydrochemical variability in the aquifers of Van Phuc. Carbon isotope signatures ($\delta^{13}\text{C}_{\text{org}}$) and C/N ratios were assessed in combination with lithology, geochemistry, hydrochemistry, hydrology and the distribution of specific biomarkers.

The relationship of C/N ratios and $\delta^{13}\text{C}_{\text{org}}$ distinguished four groups of sediment types that differ in their organic carbon sources. This includes organic carbon originating predominantly from vascular C_3 plants (C/N: 15.4-21.0, $\delta^{13}\text{C}_{\text{org}}$: -28.6 to -26.7 ‰), C_4 plants (C/N: 10.6; $\delta^{13}\text{C}_{\text{org}}$: -14.8 ‰), freshwater derived particulate organic carbon (C/N: ≤ 8 ; $\delta^{13}\text{C}_{\text{org}}$: ≤ -24 ‰) as well as mixtures incorporating both sources. At the high As sites, we found particulate organic carbon (POC) being 1 to 2 ‰ less depleted in $\delta^{13}\text{C}_{\text{org}}$ than at low As sites. More importantly, however, our assessment shows that, the availability of organic matter has to be considered decisive with regard to groundwater As contamination. Fine-grained clayey sediments overlaying sands generally protect organic matter from substantial degradation and its leaching into an adjacent aquifer. However, at the sites that are high in dissolved As n Van Phuc, sediment layers rich in organic matter are hydraulically connected to the underlying aquifer. Here, soluble organic matter seeping into the aquifer can induce and/or

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enhance reducing conditions, thereby mobilising As from Fe oxy-hydroxides. Our study shows that both the clay content as well as the origin of organic matter are largely controlled by the depositional environment of the sediments.

Keywords: arsenic, Vietnam, organic matter, $\delta^{13}\text{C}_{\text{org}}$, C/N-ratio

1 Introduction

Arsenic contamination of shallow alluvial aquifers due to geogenic processes is a well-known global problem, but it is most severe in South and Southeast Asia. Over the last 30 years, the consumption of As-rich food products and drinking water has caused serious health problems, especially in the densely populated deltas of the Ganges-Brahmaputra River system in Bangladesh and India (Nickson et al., 2000; Ravenscroft et al., 2001; McArthur et al., 2004; van Geen et al., 2006), the Mekong River, Cambodia (Polya et al., 2005; Berg et al., 2007; Buschmann et al., 2007; Rowland et al., 2007) and the Red River, Vietnam (Berg et al., 2001, 2008; Postma et al., 2007; Eiche et al., 2008; Winkel et al., 2011; van Geen et al., 2013).

Microbes play a key role in the mobilisation of As in these aquifers, either by directly reducing Fe oxy-hydroxides or by changing redox conditions through organic matter degradation (e.g. Bhattacharya et al. 1997; Nickson et al., 2000; Zobrist et al., 2000; McArthur et al., 2001; Dowling et al., 2002; Islam et al., 2004). Several studies have shown that an excess of labile organic matter can significantly increase the reductive release of As from Fe oxy-hydroxides due to the stimulation of microbial activity (e.g. Harvey et al., 2002; Gault et al., 2005; Rowland et al., 2007; Radloff et al., 2007; Mailloux et al., 2010; Neidhardt et al., 2014). Traditionally, the lability and degradability of organic matter in soils and sediments have been related to the molecular structure of components. Therefore, complex plant derived molecules, such as lignin, have been considered recalcitrant with very slow turnover rates (Philip, 1985; Hedges et al., 1985). Recent research, however, gives strong indications that this view is only valid during the early stages of degradation (up to decades) (e.g. Heim and Schmidt, 2007; Marschner et al., 2008). In the long run, nutrient limitation or

microbial accessibility determines the degradation rate. In this context, microbial accessibility is mainly controlled by the adsorption of organic matter onto mineral surfaces or its encapsulation into pores or aggregates (e.g. von Lützow et al., 2006; Ekschmidt et al., 2005; Marschner et al., 2008; Dungait et al., 2012; Jones et al., 2015).

The actual source of organic matter available to indigenous microbes is still a matter of debate and is site specific. The following internal and external sources of organic matter have been discussed in the literature: (1) *in situ* degradation products from peat layers or confining sediments (Nickson et al., 2000; McArthur et al., 2001; Dowling et al., 2002; Zheng et al., 2004); (2) the infiltration of surface-derived organic carbon of natural (soil, ponds or river beds) or anthropogenic (wastewater) origin percolating into the aquifer, a process possibly enhanced due to the extensive withdrawal of groundwater (MacArthur et al., 2001; Harvey et al., 2002; Harvey et al., 2006; Mailloux et al., 2010; Farooq et al., 2012; Ghosh et al., 2015a) and (3) thermally mature petroleum-derived hydrocarbons that seep into the aquifer from deeper zones (Rowland et al., 2006, 2007; van Dongen et al., 2008; Ghosh et al., 2015b).

Organic matter characterisation can provide crucial information about its source and depositional environment as well as possible diagenetic changes after it is deposited (Lamb et al., 2006; Quicksal et al., 2008). Specific molecules (such as hopanes, steranes, n-alkanoic acids, n-alkanols and sterols) or their specific ratios, such as the carbon preference index (CPI) and average chain length (ACL), have been used in the past to characterise the origin and degradation state of organic matter (Rowland et al., 2007; Anawar et al., 2010; Al Lawati et al., 2012; Ghosh et al., 2015a, b). The determination of these individual compound classes is very specific and time consuming, which limits the number of samples that can be analysed. In this context, the $\delta^{13}\text{C}_{\text{org}}$ and C/N ratios of sedimentary organic matter are bulk parameters, which can be more easily obtained. The isotopic signatures of organic carbon reflect the primary source of organic matter in the sediment. Vascular plants using the C_4 photosynthetic pathway generally have $\delta^{13}\text{C}_{\text{org}}$ signatures in the range of -16 to -12 ‰ (Fry and Sherr, 1984). The $\delta^{13}\text{C}_{\text{org}}$ signature in vascular C_3 plants is strongly depleted in -28 to -26

‰ (Table 1) with the most depleted $\delta^{13}\text{C}_{\text{org}}$ values (-31.3 to -24.5 ‰) found in coastal and salt-tolerant C_3 plants (mangrove trees, marsh and bog plants of the temperate zone) (Hornibrook et al., 2000; Marchand et al., 2005; Muzuka and Shunula, 2006; Ranjan et al., 2011). The organic carbon of marine particulate organic matter (algal and bacterial cells, organic detritus) typically has $\delta^{13}\text{C}_{\text{org}}$ signatures in the range of -22 to -19 ‰ (Fry and Sherr, 1984; Meyers, 1994). The isotopic composition of particulate organic matter (Table 1) deposited in freshwater environments (bacteria, algae, plant detritus or soil) has a similar range of values as terrestrial organic matter ($\delta^{13}\text{C}_{\text{org}}$, Lamb et al., 2006). The mixing of C_3 and C_4 plant material leads to similar results as those obtained with marine material, which makes interpretations less specific. Hence, $\delta^{13}\text{C}_{\text{org}}$ vs. C/N ratios are plotted to indicate primary organic matter sources. Furthermore, sediment diagenesis (e.g. the preferential decay of marine derived organic matter) or relocation can alter the isotopic signature (McArthur et al., 1992; Lamb et al., 2006; Ghosh et al., 2015a, b).

Measuring C/N ratios alongside $\delta^{13}\text{C}_{\text{org}}$ values often strengthens interpretations because this ratio is also source specific (Lamb et al., 2006). Terrestrial OM is dominated by nitrogen-depleted or nitrogen-free molecules, such as cellulose or lignin, leading to high C/N ratios (>15) (Table 1). Marine-derived organic matter contains more nitrogen-rich proteins, which result in much lower C/N ratios (5 to 12) (Table 1, Hedges et al., 1986; Lamb et al. 2006). However, decomposition, especially in the early stages of deposition, can severely alter the C/N ratio and $\delta^{13}\text{C}$ due to the preferential degradation of certain molecules (Lamb et al. 2006, Manzoni et al., 2008). In combination, however, $\delta^{13}\text{C}_{\text{org}}$ signatures and C/N ratios are regarded as reliable parameters for source identification in fluvio-deltaic sedimentary environments (Hoefs, 2009) and have widely been applied to reconstruct organic matter sources. More details on the application of both parameters can be found in the comprehensive review by Lamb et al. (2006).

Many authors have highlighted the importance of (labile) organic carbon in triggering reductive As dissolution in Southeast Asia (e.g. Harvey et al., 2002; Mailloux et al., 2010; Postma et al., 2010; Neidhardt et al., 2014), yet only a limited number of studies have truly

characterised the composition of organic matter in As-affected aquifers (Rowland et al., 2006, 2007; Anawar et al., 2010; Al Lawati et al., 2012; Neidhardt et al., 2013, Ghosh et al., 2015a, b). The area around Van Phuc, Vietnam, is characterised by adjacent aquifers with highly contrasting hydrochemistry and redox-conditions (Eiche et al., 2008; van Geen et al., 2013). Low levels of dissolved As are accompanied by sub-oxic conditions, whereas high dissolved As concentrations are coupled to highly reducing environments. The facts that the aquifer sands are overlaid by a massive clay aquitard (10 to 23 m thick) and the groundwater age (>15 years) imply slow recharge of labile organic matter in Van Phuc aquifers largely from *in situ* sources (van Geen et al., 2013). We assume that the patchy As distribution is, at least in parts, caused by differences in the origin of *in situ* organic matter and its composition. This, in turn, is influenced by the depositional history of the sediments. We tested these hypotheses by combining our results for TOC, C/N and $\delta^{13}\text{C}_{\text{org}}$ measurements from a transect in Van Phuc with the previously described lithology, geochemistry, hydrochemistry, hydrology (Eiche et al., 2008; Van Geen et al., 2013) and distribution of specific biomarkers (Al Lawati et al., 2012).

2 Geological Setting

The Red River Delta is the fourth largest delta in Southeast Asia (Tanabe et al., 2006) and comprises an area of ~14,000 km² (Luu et al., 2010). The whole Red River Basin stretches from 20°00' to 25°30' N and from 100°00' to 107°10' E (Berg et al., 2001). Present and past morphology, as well as the Quaternary geology of the delta plain (Figure 1), indicate the highly variable discharge of the Red River over the past millennia, mainly in response to eustatic sea level changes that have led to the erosion and accumulation of alluvial material due to frequent riverbed movement. These processes were superimposed by a succession of transgression and regression periods since the last glacial maximum that also brought in material of marine origin (Tanabe et al., 2006; Weinman, 2010). The boundary between fluvial- and marine-dominated depositional environments has shifted since the last cold phase in response to eustatic sea level changes (Tanabe et al., 2003a). The marine

influence during the Quaternary period, however, has never progressed further inland than Hanoi (Tanabe et al., 2003a). Within the Holocene clay deposits, organic rich layers (mainly referred to as peat) are common (Mathers et al., 1996). These result from the development of large mangrove flats between 9 and 4 cal. kyr BP as a result of the overall sea-level rise, which is sometimes even above the present-day sea level (Tanabe et al., 2003b). The multitude of processes that occurred have made the lithology of the Red River Delta highly complex and highly variable within short distances. Notably, some of the peat can be missing entirely in certain areas (Figure 1).

Around Hanoi, the Quaternary sequence has a thickness of 50 to 100 m (Mathers et al., 1996; Mathers and Zalasiewicz, 1999). This sequence contains several aquifer units, which are of great importance as drinking water sources. The lower aquifer system is highly permeable and is, therefore, used as the main source for Hanoi's water supply (Trafford et al., 1996). In 2005, 10 major well fields extracted ~650,000 m³/day (Berg et al., 2008), leading to depression cones of up to 30 m (NHEGD, 2002). The heavy pumping continues due to increasing water demand. This has induced changes in natural groundwater flow paths (Winkel et al., 2011; van Geen et al., 2013).

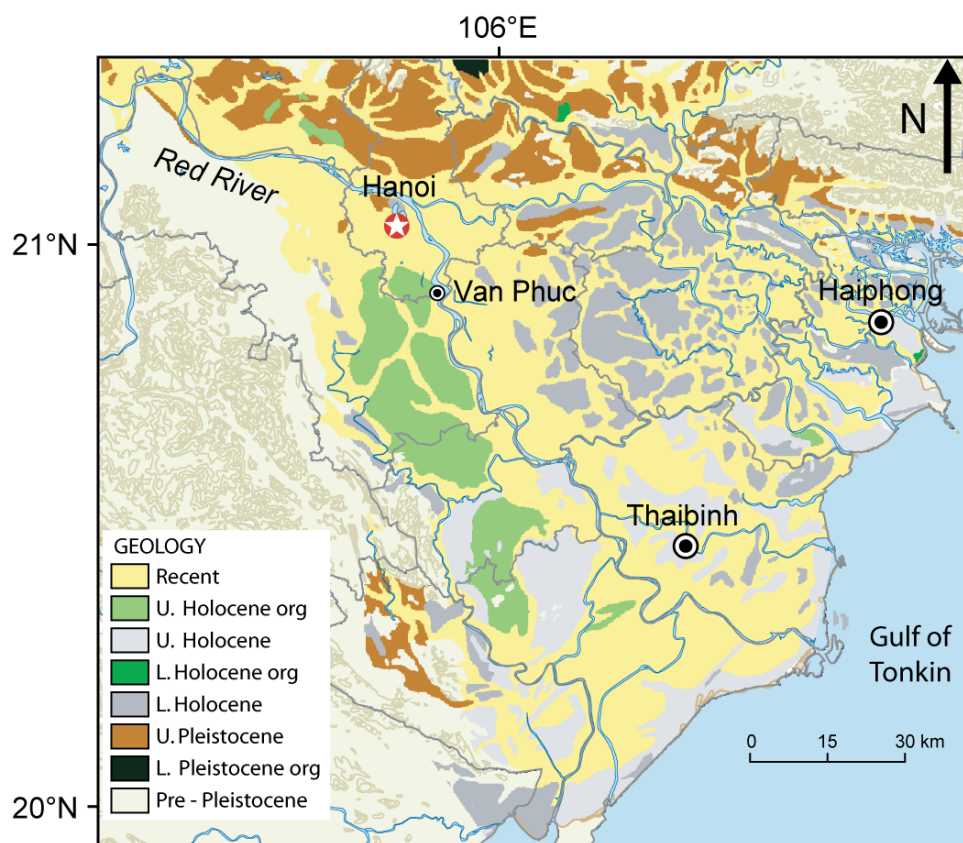


Figure 1: Geological map of the Red River Delta, depicting the distribution of Holocene, Pleistocene and recent sediments (U. = upper, L. = Lower, org. = organic rich). Modified from the Vietnam Geological Survey (1998).

3 Material and Methods

3.1 Study site

The study site, Van Phuc village, is situated ~10 km southeast of Hanoi (Figure 2). The site is located inside a large meander belt on one side and a dyke that protects the south-western parts of Hanoi from annual flooding on the other side. Consequently, the village itself occasionally floods for a few days during the rainy season. The aquifer of Van Phuc consists of a loose bedding of Holocene and Pleistocene sediments, and it reaches a depth of more than 40 m. It is overlain by a clay cap, which has variable thickness, depending on the distance to the river bed (Weinman, 2010; van Geen et al., 2013). The groundwater level responds rapidly to the daily and seasonal fluctuations of water levels in the Red River. The aquifer is, at least in part, recharged by river water to the southeast of Van Phuc village.

172 Groundwater ages of more than 15 years in the aquifer, however, point towards low recharge
 173 rates (van Geen et al., 2013).

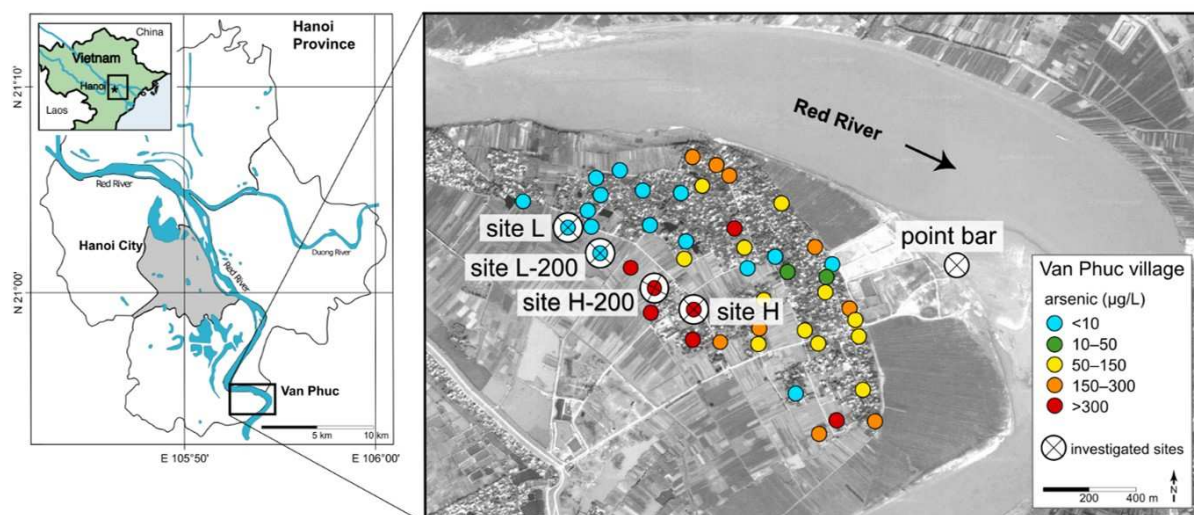


Figure 2: The study site Van Phuc is located 10 km southeast of Hanoi (picture, left). The distribution of dissolved As in Van Phuc is heterogeneous with areas of high and low As concentrations directly next to each other (picture, right). Sediments used in this study were taken along a transect from the low to the high As areas in Van Phuc. Additionally, a point deposit was also investigated. A more detailed overview of the geochemistry of sites L (low As) and H (high As) is described in Eiche et al. (2008). Groundwater and sediment samples from site H-200 and site L-200 were taken with a needle sampler device (Weinman, 2010; van Geen et al., 2013) (modified based on Eiche et al., 2008).

174 The lithology at sites L (low As) and H (high As) was described in detail in Eiche et al.
 175 (2008). The most important facts will be briefly summarised here. Based on grain-size
 176 analysis, the sediment at site L can be separated into three distinct layers: a Holocene
 177 aquitard extending to a depth of 23 m, a sandy Pleistocene aquifer extending to a depth of
 178 48 m and a Pleistocene gravel aquifer starting at a depth of 54 m (where drilling stopped).
 179 Noteworthy are two distinct, black, organic-rich intervals at depths of 11 to 13 m and $18.5 \pm$
 180 0.1 m (Figure 3) within the aquitard. The transition between the aquitard and the underlying
 181 aquifer (23 m) is marked by Fe-concretions consisting of goethite and quartz. The aquitard is
 182 characterised by strong variations in colour (brown, green, grey, white and black), indicating
 183 differences in the geochemistry of the sediment. In contrast, the aquifer material is mainly
 184 orange-brown to brown in colour.

185 The Holocene aquitard at site L-200 (200 m away from site L) extends to a depth of 16
 186 m. The sediment is orange-brown to brown throughout the whole profile, indicating oxic to

suboxic conditions (Figure 3). The transition between the Holocene clay aquitard and the sandy aquifer at site H-200 (200 m away from site H) coincides with a change in colour from brown to grey at 13 m (Weinman, 2010). The lithology at site H differs significantly from that at site L and is more heterogeneous. The Holocene aquitard is only 13 m thick, and the colour changes from reddish-brown to greyish at a depth of 7 m, indicating reducing conditions (Figure 3). Below that, alternating clayey silt, silty fine sands and fine sands occur to a depth of 21 m. Further down, a Holocene sandy aquifer follows to a depth of 55 m, where the Pleistocene gravel aquifer is present.

3.2 Sediment sampling

In April 2006, two ~55-m-long sediment cores were retrieved by rotary drilling at site L, located in the low-arsenic area, and at site H, located in the high-arsenic area (Figure 2). The distance between the two sites is approximately 700 m. Samples (~100 g) were taken from the sediment cores at intervals of 1 m, and more frequently, in cases of significant changes in colour, grain size or texture. Sediment material (~20 to 30 g) from two locations (Site L-200, VPNS4, and Site H-200, VPNS3) along a transect between sites L and H (Figure 2) was provided by Weinman (2010). These two sites are referred to as VPNS4 and VPNS3, respectively by Weinman (2010). The authors simultaneously sampled pore water and sediment with a needle sampler device (van Geen et al., 2006, 2008; Weinman, 2010). Site L-200 is close to site L (~200 m away) and site H-200 is close to site H (~200 m distance). Additionally, one sample was collected from a recent point bar deposit, which is used for sand mining (Figure 2). The sediments were placed in polypropylene bags and flushed with N₂ to minimise oxidation between sampling and analysis. Before transport, the samples were packed into Mylar bags and flushed again with N₂ to avoid oxidation and alteration of the sediment. The samples were sent to Germany where they were frozen for further analysis. Both C/N and isotope analysis require powdered samples. Therefore, sub-samples of the sediment core were dried at 40 °C and ground to powder prior to analysis.

3.3 Carbon and nitrogen analysis

The total carbon content of bulk sediment material from sites L and H was quantified using a Carbon-Sulphur Analyser (CSA 5003, Leybold Heraeus, Germany). The inorganic carbon content was determined with a Carbon-Water Analyser (CWA 5003, Leybold Heraeus, Germany). The total organic carbon content (TOC) was calculated by subtracting the inorganic carbon from the total carbon. The total nitrogen (TN) in these samples was measured with an elemental analyser (EA; EuroEA300, Euro Vector). The TN and TOC measurements of decarbonated samples from the needle sampler sediments (L-200 and H-200) were carried out with an elemental analyser (EuroEA3000, HekaTech). The reference standards BBOT (HekaTech) and GBW 07403 (Office of CRN's China) were included to check accuracy (N: <10%, C: <3%). Reproducibility was determined through repeated measurements of these standards (N: $\pm 17\%$, C: $\pm 2\%$). The results of TOC and TN measurements were used to calculate the molar C/N-ratio.

3.4 Isotopic analysis of organic carbon

Samples with sufficient organic carbon for isotope analysis were chosen based on their TOC values. This resulted in 19 samples from site L and 24 from site H as well as 11 and 8 samples from the needle sampler sites, L-200 and H-200, respectively. Prior to analysis, inorganic carbon was removed on a hot plate using HCl (2%, p.a.). The pre-treated sediment was washed with Milli-Q water to remove the excess chloride ions. The $\delta^{13}\text{C}_{\text{org}}$ of decarbonated samples was measured using an elemental analyser (EuroEA3000, EuroVector, Italy) in continuous flow mode, which was connected to an isotope ratio mass spectrometer by an open split (IRMS: IsoPrime, Fa. GV Instruments, UK). All $\delta^{13}\text{C}_{\text{org}}$ values were reported relative to the Vienna Pee Dee Belemnite (‰ VPDB). The precision calculated from three repeated sample measurements was better than ± 0.19 ‰ for C. In some samples from site L that had very low TOC concentrations, the precision was ± 0.4 ‰. The accuracy was checked with the certified reference materials USGS24 and NBS21 for carbon (± 0.11 ‰).

Table 1: Typical $\delta^{13}\text{C}_{\text{org}}$ and C/N ranges for organic inputs from different sources combined with ranges from the four sites that were investigated within this study (POC: particulate organic carbon).

		C/N-ratio	$\delta^{13}\text{C}$ [‰]
POC	<i>Marine</i>	5 to 12 ^[1]	-22 to -18 ^[2]
	<i>Freshwater</i>	5 to 10 (12) ^{[3], [4]}	-30 to -25 ^[4]
Vascular C₃		>12 ^[4]	-28 to -26 ^[2] (-35 to -22) ^[4]
Vascular C₄		>30 ^[4]	-16 to -12 ^[2]
Site L	<i>Aquitard</i>	2.6 to 15.4	-26.8 to -14.8
	<i>Aquifer</i>	5.9 to 11	-26.6 to -24.7
Site L-200	<i>Aquitard</i>	5.3 to 21.1	-28.7 to -25.3
	<i>Aquifer</i>	3.4 to 6.7	-26.5 to -24.7
Site H-200	<i>Aquitard</i>	3.7 to 13.1	-26.3 to -22.3
	<i>Aquifer</i>	5.3 to 17.4	-26.8 to -24.6
Site H	<i>Aquifer</i>	7.1 to 10.5	-25.6 to -20.1
	<i>Aquitard</i>	5.8 to 7.8	-27.2 to -23.6

^[1]Hedges et al. (1986); ^[2]Fry and Sherr (1984); Meyers (1994); ^[3]Maybeck (1982); ^[4]Lamb et al. (2006); ^[5]Wilson et al. (2005)

4 Results

4.1 Organic carbon and C/N-ratios

The TOC concentrations clearly differed in the aquitard and aquifer sediments at site L, and higher values were mainly found in the aquitard (0.04 to 4.55 wt.%). Figure 3 shows that TOC concentrations were highest in the two black layers, with 3.10 to 4.55 wt.% at a depth of 10.8 to 13 m and 0.69 wt.% at 18.5 ± 0.1 m depth. In the aquifer, TOC concentrations ranged from 0.01 to 0.06 wt.% (mean: 0.02 ± 0.01 wt.%). At site L-200, only samples between 9 and 27 m were available. Down to a depth of 17 m, the TOC content was relatively variable at 0.13 to 3.01 wt.%. The highest concentrations were found in the clay layer at 9 m depth. At >17 m, the TOC was considerably lower (0.04 to 0.08 wt.%, Figure 3). At site H-200, the TOC ranged between 0.10 to 0.79 wt.% (mean: 0.34 ± 0.3 wt.%) at the investigated depth interval of 3 to 23 m (Figure 3). In the aquitard at site H, TOC concentrations varied considerably from 0.03 to 0.82 wt.% (mean: 0.30 ± 0.27 wt.%). Many layers still had higher

TOC content than the underlying aquifer (mean: 0.03 ± 0.01 wt.%) (Figure 3). The TOC concentration of the point bar deposit was 0.08 wt.%.

The low organic matter content in the sediment allowed determination of the molar C/N ratios for a limited number of samples. At site L, the C/N ratios varied between 2.6 – 15.4, with the highest values occurring in organic-rich layers at a depth of 12 and 18.5 m. Only two C/N ratios (5.6, 11) were available for the aquifer at site L; one of them was from a silty layer at a depth of 27 m (Figure 2). At site L-200, the C/N ratios varied between 2.5 and 21, with mean values of 4.5 ± 1.2 below a depth of 17 m. In the two organic-rich layers above, the highest C/N ratios among all samples were found at 18.3 and 21 m (Figure 2). The C/N ratios at site H-200 varied considerably, from 3.1 to 17.4. Ratios above 10 were found at a depth of 9 to 13 m, where the TOC content was highest. At 27 m, a very high C/N ratio of 17.4 was determined (Figure 2). At site H, the C/N ratios were in the range of 5.8 to 10.5, with the highest values at a depth of 12 m (Figure 3). The range of C/N ratios in aquifer and aquitard sediments is given in Table 1.

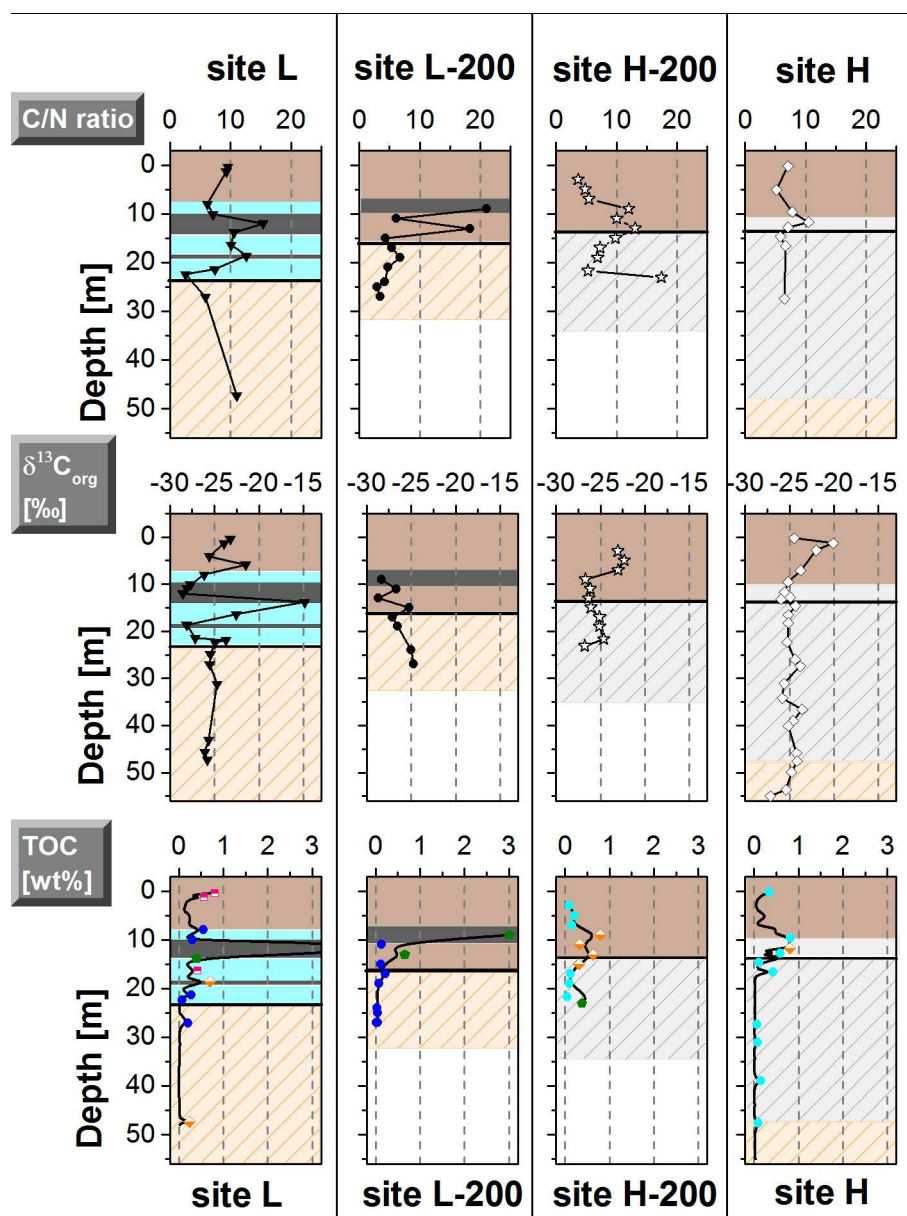


Figure 3: Depth profile of $\delta^{13}\text{C}_{\text{org}}$, C/N and TOC at all four sites. The results of the individual samples can be taken from Table S1 (supplementary content). In the background, the dominant colours (brown, cyan, dark grey, grey and orange) of different sediment layers are visible. The thick black line divides the aquitard (top) and the aquifer (bottom), according to Eiche et al. (2008), for sites L and H, and according to Weinman (2010) for site H-200 and site L-200. Based on the relationship between C/N and $\delta^{13}\text{C}_{\text{org}}$ signatures, sediments were grouped (see Figure 5). This grouping was added to the TOC depth profile (green: Group_1; blue/cyan: Group_2; orange: Group_3; pink: Group_4).

4.2 Carbon isotopic signatures ($\delta^{13}\text{C}_{\text{org}}$)

The $\delta^{13}\text{C}_{\text{org}}$ signatures of the aquitard of site L (0 to 23 m) varied considerably (Figure 3), from -28.6 ‰ (11 m) to -14.8 ‰ (mean: -24.7 ± 3.5 ‰). The most depleted $\delta^{13}\text{C}_{\text{org}}$ signatures (< -28 ‰) were found in the two black, organic-rich layers (10.8 to 13, 18.5 ± 0.1 m). On the contrary, a whitish layer at 14 m depth was characterised by the least depleted $\delta^{13}\text{C}_{\text{org}}$

signature of -14.8‰. In the sandy aquifer at site L (>23 m), the $\delta^{13}\text{C}_{\text{org}}$ signatures varied less and were in the range of -26.1 to -24.7 ‰ (mean: -25.5 ± 0.4 ‰). At site L-200, the $\delta^{13}\text{C}_{\text{org}}$ values varied between -28.7 and -24.7 ‰ (mean: -26.5 ± 1.4 ‰). Comparable to site L, the most depleted $\delta^{13}\text{C}_{\text{org}}$ signatures (<-28‰) were found in two organic-rich layers (9, 13 m). In the sandy aquifer, which started below 17 m, the highest $\delta^{13}\text{C}_{\text{org}}$ signatures were found at >-25.0 ‰ (Figure 3). Site H-200 was characterised by strongly varying $\delta^{13}\text{C}_{\text{org}}$ values in the range of -26.8 to -22.3 ‰ (Figure 3). The least-depleted $\delta^{13}\text{C}_{\text{org}}$ signatures were found near the surface at a depth between 3 and 9 m. At greater depths (>9-23 m), $\delta^{13}\text{C}_{\text{org}}$ values varied only slightly (mean: -25.8 ± 0.8 ‰). At site H, the $\delta^{13}\text{C}_{\text{org}}$ signatures were in the range of -26 to -20.1 ‰ (mean: -24.2 ± 1.7 ‰) in the aquitard (<13 m) and -27.2 to -23.6 ‰ (mean: -24.8 ± 0.7 ‰) in the aquifer (Figure 3). Note that the $\delta^{13}\text{C}_{\text{org}}$ signatures at the depth range of 1.3 to 8 m were relatively enriched (-23.5 to -20.1 ‰). The sample obtained at a depth of 55 m at site H, taken close to the Pleistocene aquifer, showed the most depleted $\delta^{13}\text{C}_{\text{org}}$ signatures, at -27.2 ‰. The point bar deposit showed a $\delta^{13}\text{C}_{\text{org}}$ signature of -24.0‰. The ranges of $\delta^{13}\text{C}_{\text{org}}$ values in aquitard and aquifer sediments at all sites are also given in Table 1.

5 Discussion

Hydrochemistry and dissolved As concentrations are heterogeneous throughout Van Phuc (Eiche et al. 2008; van Geen et al., 2013). Groundwater conditions in the sandy aquifer at site L, which is low in dissolved As (< 4µg/L), are clearly less reducing (>0 mV) when compared to the high As sites (site H / H-200). Apart from the negative redox-potential (< -120 mV) at the high As sites, the difference is also illustrated by the high concentrations of other dissolved species, indicating reducing conditions and biodegradation (Figure 4, Eiche et al., 2008; van Geen et al., 2013). For example, this includes high concentrations of dissolved Fe (10-22 mg/L), NH_4^+ (2.3-23 mg/L) and P (0.3-1.3 mg/L), which highlights again the importance of organic matter degradation for mobilisation of As by reductive dissolution of Fe oxy-hydroxides (e.g. Harvey et al., 2002; Gault et al., 2005; Rowland et al., 2007; Radloff et al., 2008; Neidhardt et al., 2014). Site L-200 exhibits transitional hydrochemical

characteristics between the L and H sites. Redox potential (<0 mV), dissolved As (<2.2 $\mu\text{g/L}$), Fe ($<<0.1$ mg/L) and P (<60 $\mu\text{g/L}$) concentrations are similar to site L, but NH_4^+ (6.3 mg/L) and HCO_3^- (501 mg/L) concentrations are comparable to H sites. There is no satisfactory explanation for why the hydrochemistry is so different along this transect. Here we were testing the hypothesis that organic matter's origin, its composition and availability and the depositional environment are important factors that control these apparent differences.

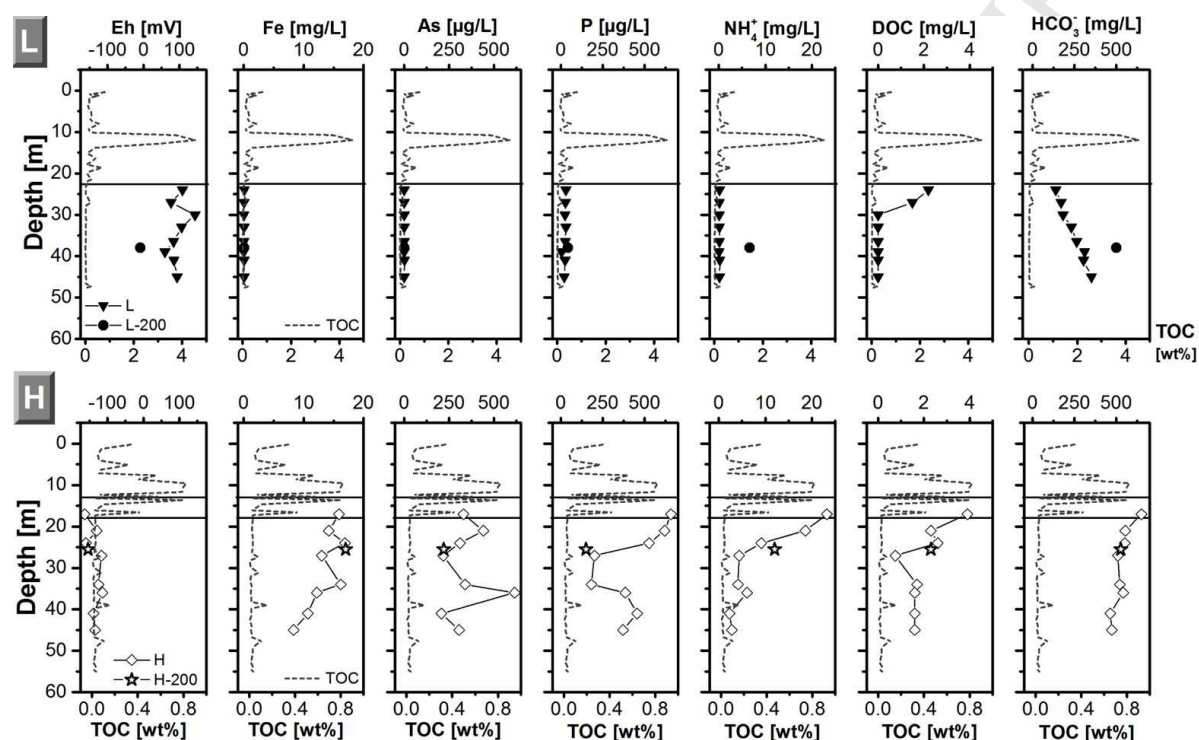


Figure 4: Depth profiles of dissolved species and sedimentary TOC at the L (top) and H (bottom) sites in Van Phuc. The dotted lines depict the TOC content in the sediment cores. The solid black lines indicate the boundary of the aquitard and aquifer.

5.1 Origin of organic matter

The origin of organic matter embedded in the sediments of Van Phuc was deduced from the relationship between C/N ratios and $\delta^{13}\text{C}_{\text{org}}$ values (Figure 5, Lamb et al., 2006). Based on this association, the individual samples were separated into four groups (Figure 4).

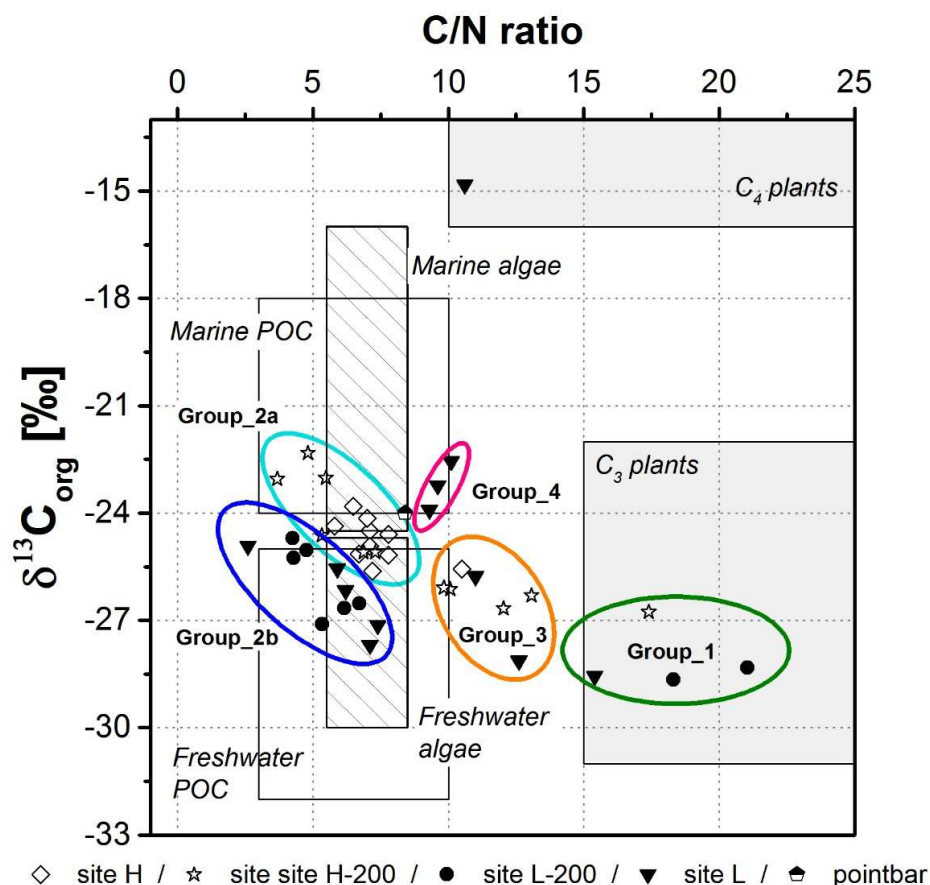


Figure 5: Grouping of sediment samples based on their relationship between the $\delta^{13}\text{C}_{\text{org}}$ signatures and C/N ratios of all four sites. In Group_1, vascular C_3 plants are the predominant carbon source. Group_2 indicates freshwater algae and particulate organic carbon (POC) as major sources of organic matter. Group_3 sediments primarily have organic carbon derived from freshwater POC and vascular C_3 plants. Group_4 consists of vascular C_3 probably mixed with C_4 plant material. Predominance fields of different sources of organic carbon are based on Lamb et al. (2006) and referenced therein.

One important source of organic matter in the sediments of Van Phuc likely originated from vascular C_3 vegetation (Group_1, Figure 5) with typical C/N ratios of 15.4 to 21.1 and $\delta^{13}\text{C}_{\text{org}}$ of -28.6 to -26.7 ‰. Furthermore, one sample is plotted in the predominance field of vascular C_4 plants (C/N: 10.6; $\delta^{13}\text{C}_{\text{org}}$: -14.8 ‰). These findings are in line with results of Al Lawati et al. (2012) who studied different biomarkers in selected sediments of L and H sites. The presence of n-alkanes with $\text{C}_{\text{max}} \geq 29$ and n-alkanols and n-alkanoic acids with $\text{C}_{\text{max}} \geq 24$ supports higher plant derived organic matter (Eglinton and Hamilton, 1963, 1967) as an important carbon source. In both studies, however, this source was only found to be

dominant in a few aquitard samples (Figure 3) that were high in TOC (0.12 to 4.55 wt.%). These organic-rich layers, often called peat, are assumed to mainly result from periods of sea-level high stand when mangrove forests were widespread around Hanoi (Mathers et al. 1996; Tanabe et al. 2006). C/N and $\delta^{13}\text{C}_{\text{org}}$ values comparable with Group_1 data were found in a recent study by Tue et al. (2012a, b) on a mangrove ecosystem in the Red River Estuary (Ba Lat). The authors reported $\delta^{13}\text{C}_{\text{org}}$ values of -28.1 ± 1.4 ‰ (leaves) to -25.9 ± 1.4 ‰ (mangrove sediments) and C/N ratios of 27.1 ± 10.4 (leaves) and 11.6 ± 2.5 (mangrove sediments), which supports the input of mangrove derived OM for the sediments in Van Phuc.

Most of the sediments, however, have C/N ratios ≤ 8 , which suggest the presence of organic matter of freshwater and marine origin (Group_2, Figure 5). The majority of all samples within Group_2 suggests the presence of freshwater POC, which can encompass phytoplankton and the detritus of terrestrial plants as well as algae (Lamb et al., 2006). The very low C/N ratios in the range of 4 to 8 in our samples, in addition to $\delta^{13}\text{C}_{\text{org}}$ values ≤ -24 ‰, however, point towards a dominance of bacteria, algae and freshwater phytoplankton in Van Phuc (Meyers, 1994; Tyson, 1995). The low C_{max} of n-alkanoic acids (C_{max} : 20) and n-alkanes (C_{max} : 20-21) in some aquifer sediments investigated by Al Lawati et al. (2012) could also be indicative of microbial or microalgal organic matter input (Simoneit, 1977). However, the alteration of the signal by OM degradation, as indicated by the CPI of n-alkanes of ≈ 1 in aquifer sediments at site L and H, has to be considered an additional process that influences the bulk parameter trends of Group_2 sediments (Clark and Blumer, 1967). The low to very low TOC (< 0.2 wt.%) of the samples in Group_2 supports the assumption that some degradation might have taken place. Al Lawati et al. (2012) concluded from the CPI ≈ 1 and the presence of an unresolved complex mixture (UCM) that petroleum derived hydrocarbons could be another organic carbon source in aquifer sediments that are low in TOC. Only three samples of Group_2a (site H-200) clearly plot within the field, which suggests marine POC is major organic matter source (Figure 5). Although it is known that transgression leads to the deposition of estuarine to subtidal muds in the Van Phuc area (Weinman, 2010; Tanabe et

al., 2003a, 2006), the presence of marine derived organic matter of autochthonous origin is only expected at the L sites (Weinman, 2010). Furthermore, no short-chained n-alkanes (C15-C19) were found by Al Latawi et al. (2012), which would support the concept of marine derived organic matter as a major source of organic carbon (Clark and Plummer, 1967). A more reasonable explanation for the marine signals would be the input of organic matter from freshwater algae in C₄ dominated catchments (Chivas et al., 2001). C₄ vegetation is widespread in the Red River Delta as maize has been a major crop for decades. Furthermore, clear indications for the presence of C₄ vegetation in the past have been found at site L (Figure 5).

Some organic-rich (TOC 0.32-0.80 wt.%) aquitard sediments (Group_3) seem to have organic matter derived from both freshwater POC and terrestrial C₃ plant origin, which is plausible for a fluvial setting such as the Red River Delta. This is indicated by depleted $\delta^{13}\text{C}_{\text{org}}$ signatures of <-25 ‰ in combination with C/N ratios of 9.8 to 13 (Figure 5, Lamb et al., 2006). Organic matter of mixed POC and terrestrial origin can also be assumed for sediments of Group_4. In contrast to Group_3, these sediments are characterised by a slightly lower C/N (9 to 10) and less depleted $\delta^{13}\text{C}_{\text{org}}$ (-23.9 to -22.6 ‰) signatures. Since Group_4 mainly consists of relatively recent sediments that were deposited after the last transgression stage (Tanabe et al., 2006; Weinman, 2010), a higher contribution of marine derived organic matter compared to Group_3 sediments is not a reasonable expectation. Rather an admixture of some C₄-derived detritus would explain the less depleted $\delta^{13}\text{C}_{\text{org}}$ values as maize (<-13 ‰, Chikaraishi and Naraoka, 2003) is a common crop that is cultivated in northern Vietnam, at least in modern agriculture. This assumption is supported by the similarity of both bulk parameters to the recent Red River point bar sediment composition (Figure 5).

5.2 Post-depositional changes and organic matter preservation

As mentioned above, variations of C/N and $\delta^{13}\text{C}_{\text{org}}$ values probably do not only result from changes in OM source and, thus, composition, but they can also be modified by organic

matter degradation (e.g. Berg and Staaf, 1987; Manzoni et al., 2008; Lerch et al., 2011). It has been described that, during the settling of POC in aquatic systems and the early stage after deposition, molecular characteristics determine the rate of decomposition (Amelung et al., 2008; Marschner et al., 2008; Schmidt et al., 2011, Zonneveld et al., 2011). This will lead to a selective loss of certain compounds and, consequently, to a change in C/N and $\delta^{13}\text{C}_{\text{org}}$ values in comparison to the original signal (Wilson et al., 2005; Blagodatskaya et al., 2011). Furthermore, the $\delta^{13}\text{C}_{\text{org}}$ value of the microbial biomass decreases relative to the substrate it is decomposing (Lerch et al., 2011). However, after early diagenetic modifications have ceased, both bulk organic matter parameters are reported to remain more or less stable over millions of years (Meyers, 1994) if they are well preserved. Based on this assumption, several authors state that the magnitude of change is normally insufficient to prevent a distinction between C_3 and C_4 plants (e.g. Byrne et al., 2001; Malamud-Roaman and Ingram, 2004; Lamb et al., 2006). It is a likely assumption for a large fluvial system, such as the Red River, where high amounts of sediments are annually deposited (≈ 130 Mio. t/a, Milliman et al., 1995), that organic matter is well preserved. It has been reported that, especially in clay-rich sediment layers, the supply of nutrients and oxygen is diminished in a way that organic matter degradation by microbes is less efficient (Schmidt et al., 2011). Additionally, it has been shown that organic molecules will be physically protected from degradation due to their encapsulation in aggregates, the adsorption to clay minerals or the formation of mineral-organic matter-complexes leading to inaccessibility for microbes and enzymes (e.g. Ekschmitt et al., 2005; Amelung et al., 2008; Kögel-Knaber et al., 2008, Zonneveld et al., 2010; Schmidt et al., 2011). This protection explains the presence of organic rich layers consisting of relatively fresh, higher plant derived organic matter overall but especially in the deeper aquitards in Van Phuc (Figure 3, Al Lawati et al., 2012). Ghosh et al. (2015a) drew similar conclusions from their study of As-affected deposits in the Bengal Delta Plain, India. They suggest that the presence of visible plant fragments and the enrichment of biomarkers in clay-rich layers at a depth of 132 to 156 m is due to the long-term preservation of organic matter in fine-grained sediments. From this, we can conclude that the large variations in TOC

content along the depth profile in the aquitard sediments of Van Phuc and thus C/N, $\delta^{13}\text{C}_{\text{org}}$ values are not controlled by degradation alone, but depend on a combination of changes in organic matter supply and deposition-controlled preservation. The situation is different within the coarse-grained sandy aquifer sediments that mainly comprise the OM of Group_2. Here, organic matter turnover rates will be fast and can even continue after deposition. This is because of sufficient nutrient supply and the considerably lower sorption capacity of silt and sand for organic matter and hence, a lack of organic matter sequestration. (Marschner et al., 2008; Zonneveld et al., 2010). This explains both the very low TOC content and the missing odd-over-even dominance in the n-alkane distribution in the aquifers in Van Phuc. Similar observations have been made in As-contaminated regions in the Bengal Delta Plain where the biodegradation of organic matter seems to be much faster in sand compared to clay layers (Ghosh et al., 2015a).

Despite the fact that some degradation has taken place since sediment deposition, our study reveals a distinct difference in organic matter source and composition. While organic matter at the low As sites mainly belongs to groups 1 and 2b, sediment organic matter in groups 2a and 3 is present at the high As sites. The difference is especially apparent within Group 2. When comparing samples with a similar C/N ratio, organic matter from the high As sites is always less depleted with regard to $\delta^{13}\text{C}_{\text{org}}$ values by 1 to 2 ‰. Although the differences in organic matter source and composition might not sufficiently explain the distribution of dissolved As in Van Phuc, the OM seems to be one part of the puzzle. To further assess to what extent differences in organic matter composition are responsible for the hydrochemical situation, degradation experiments with freshly drilled sediments are needed.

5.3 Availability of organic matter

As discussed above, organic matter enrichment at all sites is mainly connected to fine-grained sediments due to protection from degradation. However, two distinct differences between high and low As sites regarding organic enriched layers seem to be of importance.

At the low As sites, these layers are embedded within the aquitard (particularly at site L) with a relatively large distance to the aquifer (5 to 10 m, Figure 3). At the high As sites, organic matter-rich layers are not completely separated from the aquifer, as they are embedded within a transition zone of silt and fine sand (Figure 3, Eiche et al. 2008). In contrast, the majority of samples exhibiting TOC > 0.1 wt.% at the low As sites are present in layers of \geq 90% clay and silt, which supports the important role of organic matter sequestration. In particular, the formation of clay-organic matter complexes as a result of the high sorption affinity of clay minerals for organic matter, which are reported to severely diminish organic matter degradation, could be significantly higher at the low As sites where the clay content of TOC-rich layers is mainly \geq 8 wt.% in contrast to 4 to 8 wt.% at the high As sites. Consequently, organic matter at the high As sites is probably more accessible for microbes compared to the low As sites, due to the much lower affinity of organic matter for silt and sand (von Lützow et al., 2007).

McMahon (2001) showed that sufficient soluble organic matter, such as organic acids or humic substances, are produced in silty layers, which are more abundant at the high As sites and might migrate into the underlying aquifer. Consequently, these leached by-products could play a decisive role in inducing and maintaining reducing conditions at the high As sites. The assumption that dissolved organic matter is leaching from the aquitard is supported by the depth profiles in Figure 4. While species derived from biodegradation, such as e.g. NH_4^+ , PO_4^{3-} , HCO_3^- and DOC as well as dissolved Fe, are highest in the upper part of the aquifer at site H and similarly at site H-200, their concentrations are distinctly lower throughout the aquifer at site L (Figure 4).

5.4 Influence of depositional environment on dissolved As distribution

As discussed above, the origin, preservation and availability of organic matter show differences between the L and H sites. In each case, the depositional environment of the sediments is decisive and differs between high and low As sites. According to Weinman (2010), aquitard sediments at site L are the result of sediment deposition during

transgression periods, leading to a succession of clay-rich sub-tidal, tidal and estuarine muds in the depth range of 10 to 23 m. The fact that Holocene sands are missing at the L sites in contrast to the H sites strongly suggests that aquitard sediments at site L can be considered to be paleointerfluvial deposits, which were situated between former river channels and, consequently, were not influenced by riverbed migration in the Holocene. These fine-grained muds, which consist of mangrove-derived TOC-rich layers deposited during sea-level high stand seem to have a high potential for organic matter sequestration and, thereby, protect the underlying aquifers from the infiltration of dissolved organic carbon. This assumption is in accordance with McArthur et al. (2008), who stated that areas beneath paleointerfluvial deposits, such as palaeosols, are As free due to protection from downward-migrating As and/or organic carbon. van Geen et al. (2013) classified clay layers deposited at 12 to 17 m depth in the low As area in Van Phuc as palaeosols, which resulted from the last sea-level low stand. This is in line with our results where a protective layer is an important prerequisite for low As levels in these aquifers.

The sediments at the high As sites, on the other hand, were characterised as fluvial facies by Weinman (2010) and were deposited as part of a migrating palaeochannel system. The dominance of fluvial sediments is in accordance with our study, where we found a close similarity in C/N ratios and $\delta^{13}\text{C}_{\text{org}}$ signatures between the H sites (Group 2a) and the point bar deposit (Figure 4). Furthermore, organic-rich layers in the aquitard, which mainly belong to Group_3, indicate mixed POC and terrestrial OM input, which is typical for fluvial settings. Moreover, there are no signs for mangrove-derived organic matter at the low As sites. The fluvial origin of the sediments also explains the higher content of silt and occasional layers of fine sand in the aquitards at the H sites. This is the reason why organic matter is more easily available for microbial degradation compared to the L sites and, consequently, why considerable downward migration of electron donors is taking place. The assumption that the sediments around site H might be the young infill of a former palaeochannel is further supported by the distribution of dissolved As and other

hydrochemical parameters along the transect between sites L and H (Weinman, 2010; van Geen et al., 2013), which delineate the extension of the palaeochannel.

6 Conclusions

Our study shows that the composition of sedimentary OM and its origin is different between high and low As sites and may partly explain the hydrochemical differences in Van Phuc. More importantly, the sequestration of organic matter within the sediments and, thus, its availability for biodegradation needs to be considered with regard to As contamination in aquifers not only in Van Phuc but also globally. In this context, the presence of substantial clay depositions overlaying the aquifers will be important. Fine-grained sediments will protect organic matter from substantial degradation and further prevent excessive leaching of electron donors into adjacent aquifers. Our study shows that both the clay content as well as the origin of organic matter is largely controlled by the depositional environment of sediments. Consequently, it can be deduced that the As contamination of aquifers in delta systems can partly be attributed to their depositional history.

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Highlights

- Particulate organic carbon (POC) from C₃/C₄ plants and freshwater is a main source of OM
- $\delta^{13}\text{C}_{\text{org}}$ values of POC in sediments from high As sites are less depleted by 1 to 2‰
- Positioning and protection of organic matter in clayey sediments is decisive for As contamination