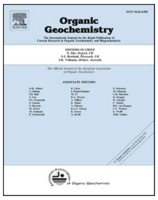
Organic Geochemistry 198 (2024) 104886

Contents lists available at ScienceDirect

Organic Geochemistry

journal homepage: www.elsevier.com/locate/orggeochem



Characterisation of dissolved organic matter in two contrasting arsenic-prone sites in Kandal Province, Cambodia

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ARTICLE INFO

Associate Editor: Ryan Pereira

Keywords:
Dissolved organic matter
Cambodia
Kandal Province
Optical properties
FT-ICR MS
As-cycling

ABSTRACT

Aquifers throughout Asia are impacted by the release of geogenic arsenic (As) into groundwater by microbial reduction of As-bearing Fe(III) (oxy)hydroxide minerals, severely impacting water quality. Groundwater dissolved organic matter (DOM) is likely key to As release, mainly as electron donor or electron shuttles. This study used optical analyses and ultra-high resolution mass spectrometry to examine the sources and composition of groundwater DOM in the As-prone aquifers of Kandal Province, Cambodia, at boreholes with differing host lithology (clay- and sand-dominated). Groundwater and surface water DOM composition were related to As concentrations, to infer the potential role of DOM in promoting As release. Optical and molecular-level analyses indicated an overall dominance of terrestrial-derived DOM in the groundwater samples, with higher freshness index and relative abundance (RA) of aliphatic compounds in clay compared to sand-dominated lithology. Compared to surface water, groundwater DOM had relatively lower O/C ratios and nominal oxidation state of carbon (−0.19 to −0.13 compared to 0.04 for ground and surface water, respectively), with a lower %RA of aliphatic compounds and higher %RA of carboxyl-rich alicyclic molecules, suggesting microbial processing of DOM since percolation into the aquifer. Concentrations of As across both sites were negatively correlated with DOM tryptophan:fulvic-like fluorescence and the %RA of aliphatics, potentially indicating microbial degradation of biolabile DOM in connection with As release, which is consistent with its role as an electron donor source. Together these data support DOM composition as an important control on microbial mediated As release.

1. Introduction

The contamination of drinking water with arsenic (As) is associated with a range of health problems including cancers, cardiovascular disease, and skin lesions (Hughes et al., 2011). Up to 220 million people worldwide are estimated to be at risk of chronic As exposure (Podgorski & Berg, 2020). The problem is especially severe in south and southeast Asia, where As-contaminated groundwater can be the primary source of drinking water. The problem is so widespread it has been termed *"the largest mass poisoning of a population in history"* (Smith et al., 2000). The As-prone aquifers are found within the Indus, Ganges, Irrawaddy, Mekong and Red River deltas, and the Hetao and Jianghan alluvial plains, all of which drain from the Himalayas. These deltas and alluvial plains consist of sediments containing As-bearing Fe(III) (oxy)hydroxide minerals (Kinniburgh and Smedley, 2001; Fendorf et al., 2010; Mukherjee et al., 2012). Arsenic is thought to be released from these minerals by microbially mediated reductive dissolution of the ferric host minerals (Islam et al., 2004; Charlet & Polya, 2006). Key to this process are the composition and environmental sources of (organic) electron donors. However, organic matter (OM) composition and environmental

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https://doi.org/10.1016/j.orggeochem.2024.104886
Received 17 May 2024; Received in revised form 16 October 2024; Accepted 16 October 2024

sources in aquifers depend on a number of site-specific factors (e.g., geomorphological setting and sediment lithology), and the impact of these factors on As release remains poorly understood (Moore et al., 2023). Proposed sources of OM in As-prone aquifers include: 1) drawdown of terrestrial-derived OM (e.g., overlying plant matter) by the hydraulic gradient maintained by pumping, with possible anthropogenic inputs (Harvey et al., 2002; van Dongen et al., 2008; Neumann et al., 2010; Whaley-Martin et al., 2016); 2) OM derived from the sediments, either deposited with the sediments or transported from upstream (McArthur et al., 2004; van Dongen et al., 2008); and 3) upwelling of thermally mature hydrocarbons (e.g., petroleum) from underlying reservoirs (Rowland et al., 2006, 2009; van Dongen et al., 2008; Al Lawati et al., 2012, 2023; Ghosh et al., 2015; Magnone et al., 2017). Sediment microcosm-based studies have shown that the type and biolability of organic material, not necessarily the total quantity, can influence the prevalence and mechanism of Fe(III) reduction and As release (Rowland et al., 2007, 2009; Glodowska et al., 2020; Qiao et al., 2020; Wang et al., 2021). Therefore, understanding how the composition and environmental sources of aquifer OM relate to As release is of key importance.

To date, research has been predominately conducted on the sedimentary OM (SOM) of As-prone aquifers (McArthur et al., 2004; Rowland et al., 2006, 2007, 2009; van Dongen et al., 2008; Al Lawati et al., 2012; Al Lawati et al., 2013; Neumann et al., 2014; Magnone et al., 2017; Ye et al., 2017; Mao et al., 2018; Pracht et al., 2018). As such, the understanding of the relationship between dissolved organic matter (DOM) composition and As release remains incomplete (Qiao et al., 2021). Biolabile DOM compounds could play a role as electron donors and carbon sources (Ghosh et al., 2015; Qiao et al., 2021) whilst more stable compounds (particularly humic compounds) may act as electron shuttles (Nevin & Lovley, 2002; Rowland et al., 2007; Mladenov et al., 2010; Melton et al., 2014; Chen et al., 2017; Kulkarni et al., 2017; Richards et al., 2019b). Furthermore, dependent on composition, DOM can undergo complexation reactions with As and iron (Fe; Mukhopadhyay & Sanyal, 2004; Guo et al., 2011; Fakour & Lin, 2014; Xue et al., 2019), and act as competitive sorption with As for sites on Fe oxide minerals (Grafe et al., 2002; Ko et al., 2004; Bauer & Blodau, 2006). Given these interactions, it is important to understand how DOM composition and source impacts As release.

The composition of DOM can be characterised by analysis of optical properties, for instance specific ultraviolet absorbance at 254 nm ($SUVA_{254}$) is used as a proxy for DOM aromaticity (i.e., greater $SUVA_{254}$ indicates greater aromaticity; Weishaar et al., 2003). In excitation emission matrix (EEM) analysis, specific excitation and emission wavelengths correspond to the fluorescence properties of DOM (Leenheer & Croué, 2003). These properties can be identified by peak-picking or deconvolution of target EEMs (e.g., for protein-like and humic-like components), accompanied by the calculation of indices (Tye & Lapworth, 2016; Richards et al., 2019b). For example, fluorescence index (FI) and Freshness index, have been related to source and processing of DOM, where higher values indicate greater relative contributions of recently produced, microbially derived OM, over processed, terrestrial OM sources (e.g., soil and vegetation; McKnight et al., 2001; Parlanti et al., 2000; Wilson & Xenopoulos, 2009; Kulkarni et al., 2017). These measurements have become widely used for the characterisation of DOM, including in studies of As-prone aquifers, due to their ease of measurement and cost-effectiveness (Derrien et al., 2019).

Ultra-high resolution Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS), allows for the molecular-level identification and categorisation of thousands of organic compounds, and is considered the most powerful technique for DOM characterisation (Hertkorn et al., 2007; Hockaday et al., 2009; Ohno et al., 2010; Dittmar & Stubbins, 2014; Spencer et al., 2014; Hodgkins et al., 2016; Derrien et al., 2019; McDonough et al., 2022). FT-ICR MS has been applied to the study of DOM in As-prone aquifers in the (Bangladeshi) Bengal Basin (Pracht et al., 2018), the Jianghan Plain (Du et al., 2020; Yu et al., 2020), and Hetao Basin (Qiao et al., 2020, 2021). The combined use of optical and FT-ICR MS techniques has been applied to aquatic environments to understand the source and composition of DOM, as well as relationships between fluorescence properties and molecular composition (e.g., Stubbins et al., 2014; Kellerman et al., 2015, 2018; Wagner et al., 2015). However, few studies have assessed this relationship in As-prone aquifers (Gao et al., 2023; Li et al., 2024; Pracht et al., 2018; Qiao et al., 2020, 2021; Wang et al., 2023), thus the association between DOM composition and As-cycling remains poorly defined. Previously, incubation studies have used FT-ICR MS to link molecular-level DOM composition to biolability (Spencer et al., 2015; Textor et al., 2018; Kellerman et al., 2018). For instance, D'Andrilli et al. (2015) proposed the molecular lability boundary (MLB), whereby organic molecules with H/C ratios ≥ 1.5 (i.e., aliphatics) were considered most biolabile. Incubation studies of water-extracted sedimentary organic matter (WESOM) from the Hetao Basin, have shown these high H/C compounds (including carbohydrate, and protein-like compounds) are microbially degraded, and associated with Fe(II) and As release from sediments (Qiao et al., 2020). Furthermore, analysis of the optical and molecular properties of the Hetao Basin has shown positive correlations between groundwater As concentrations and more biostable DOM (e.g., humic-like components and lower H/C molecular formulae), suggesting degradation of biolabile DOM coupled with reduction of As-bearing Fe (III) oxyhydroxide minerals and As release, possibly enhanced by the microbial utilisation of stable molecules as electron shuttles (Qiao et al., 2021). Incubation experiments on aquifer organics from Bangladesh have shown similar trends; particularly, the sequential degradation of organic molecules in order of decreasing nominal oxidation state of carbon (NOSC; an index for thermodynamic viability and energy potential of the organic compounds (LaRowe & van Cappellen, 2011) in connection with As release (Pracht et al., 2018). Together, these studies highlight that the combined analysis of DOM by optical and molecular techniques in As prone aquifers can provide useful insight into DOM composition, source and processing in relation to As release, highlighting the role of bioavailable DOM in microbial mediated As release.

The aquifers of the Kandal Province, Cambodia, have been characterised extensively in previous studies (Polya et al., 2005; Charlet & Polya, 2006; Rowland et al., 2007, 2008; Tamura et al., 2007; Benner et al., 2008; Kocar et al., 2008, Kocar et al., 2014; Polizzotto et al., 2008; van Dongen et al., 2008; Lawson et al., 2013, 2016; Richards et al., 2016, 2017, 2018, 2019a, 2019b; Magnone et al., 2017, 2019; Uhlemann et al., 2017). High spatial heterogeneity has been found in groundwater As, Fe, and bulk dissolved organic carbon (DOC) concentrations, in the ranges of 11–1095 μg/L, 0–6.9 mg/L, and 0.8–18 mg/L, respectively (Richards et al., 2017). Groundwater abstraction in the region is limited due to relatively low population density and economic development (Richards et al., 2018 – and references therein). Studies related to the SOM have shown that the clay-dominated sediments have higher OC content and OM is primarily derived from recently produced terrestrial sources (i.e., plant matter), compared to sand-dominated sediments where a greater proportion of OM may be derived from thermally mature (petroleum derived) hydrocarbons (Rowland et al., 2007; van Dongen et al., 2008; Magnone et al., 2017). Optical characterization of DOM at both sand and clay-dominated sites has shown an overall dominance of terrestrial-derived DOM (i.e., humic-like fluorescence properties; Richards et al., 2019b). Despite this similarity, there are indications of higher biolability of DOM in the clay-dominated area compared to that of the sand-dominated (Richards et al., 2019b), which may result in variability in As release. Comprehensive isotopic-based hydrogeological studies of the area have shown that the inorganic carbon derived from dissolved organic carbon (DOC) degradation (associated with As release and other processes) pre-dates modelled groundwater flow (by hundreds of years) and suggested the importance of in situ oxidation of DOC in As release (Magnone et al., 2019). This indicates that DOM may play an important role in As release at these sites. However, there is currently little understanding of the molecular-level composition of groundwater organics from these sites.

The aims of this study were to: (i) investigate the relationships between molecular-level and optical properties of groundwater DOM in the As-prone aquifers of Kandal Province, Cambodia; (ii) to provide insights into the potential environmental sources of the DOM and its subsequent microbial processing; and (iii) identify connections between DOM composition and As release. To achieve this, groundwater DOM composition was assessed at boreholes ($n = 8$) with differing lithology (clay- or sand-dominated) and compared to surface water DOM ($n = 1$). The composition of DOM at these sites was characterised using optical and, for the first time, molecular-level analysis from ultrahigh resolution 21 Tesla FT-ICR MS. Multivariate statistics were used to relate bulk and molecular-level DOM composition to DOC concentrations and inorganic geochemistry published elsewhere (from Bassil et al., 2024), ultimately providing insight into the role of DOM in As cycling.

2. Materials and Methods

2.1. Site Description and Field Sampling

The field sites for this study were located between the Mekong and Bassac Rivers, in Kandal Province, Cambodia. The two sites were contrasted by local stratigraphy, with one being sand-dominated and one clay-dominated (Uhlemann et al., 2017). Four 18 m deep boreholes (with 5 m of screening) ~ 2–3 m apart, were drilled at each site in January 2019 and fully developed in May 2019 (Bassil et al., 2024). These boreholes are located near sample sites along hydrogeological transects from previous studies in the area (Richards et al., 2016, 2017, 2018, 2019a, 2019b; Magnone et al., 2017, 2019), with the boreholes of the clay-dominated site being located near previously-named sites LR12–LR14 and the boreholes of the sand-dominated site near LR01 (Fig. 1). Fieldwork for this study was conducted in January 2020, with the groundwater from each well pumped to the surface using a submersible pump (Proactive Environmental Products Tornado 12-volt). Prior to sampling, each well was flushed until the oxidation–reduction-potential readings were stabilised. Water samples for DOC concentration, inorganic geochemistry (As and Fe) and DOM compositional analyses were taken from all eight boreholes, as well as a surface water sample ($n = 1$) from a lake near the boreholes of the clay-dominated site (Fig. 1).

Inorganic geochemical and DOC analyses were performed and the results thereof are discussed separately (Bassil et al., 2024). Briefly, groundwater samples were filtered through 0.45 μm cellulose filters, and transported and stored (at 4 °C) to the Manchester Analytical Geochemistry Unit (MAGU). The As and Fe concentrations were determined by inductively coupled plasma mass spectrometry (ICP-MS) after acidification with 2% v/v HNO_3, using established methods (Richards et al., 2017; Bassil et al., 2024). Bulk DOC concentrations were measured using a Shimadzu TOC-V CPN Analyser at MAGU using standard protocols (Richards et al., 2017; Bassil et al., 2024). Sampling for DOM composition analysis was conducted alongside DOC and inorganic geochemistry. Briefly, samples for EEM analyses were taken by filtration of 20 mL of sample water through 0.45 μm MERK cellulose nitrate filters using a BD-plastic syringe, into acid-washed (10% HNO_3 $\geq$ 24 h) and pre-combusted (430 °C; >3 h) amber glass vials (Richards et al., 2019b). Samples were stored at 4 °C in the dark. Similarly, for FT-ICR MS analysis, 200 mL of sample water was filtered through pre-combusted 0.7 μm Whatman GF/F filters, using a pre-combusted (430 °C, >3h) and pre-rinsed glass pump filtration system, into 250 mL acid-washed (10% HCl for 72 h) and pre-rinsed polycarbonate bottles. Samples were stored frozen (−20 °C) in the dark.

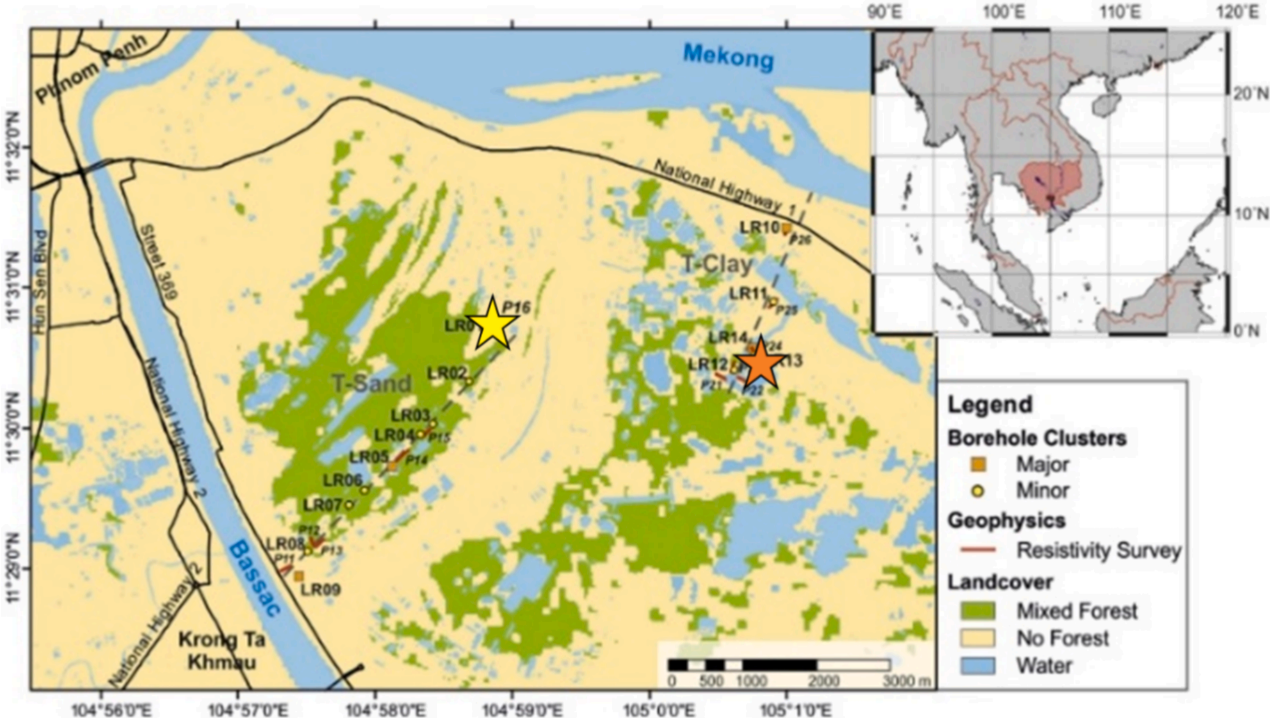


Fig. 1. Location of the boreholes in Kandal Province, Cambodia, drilled in January 2019 and sampled in January 2020 for this study and parallel studies (Bassil et al., 2024). Yellow star marks the boreholes of the sand-dominated site (n = 4), orange star marks the boreholes of the clay-dominated (n = 4) site. LR marks transects of previous hydrogeochemical surveys in the area (from 2014 to 2015), including EEM data (Magnone et al., 2017, 2019; Richards et al., 2017, 2018, 2019b) and previous electrical resistivity surveys (Uhlemann et al., 2017). Adapted from Richards et al. (2017). The surface water sample was collected from a lake near the boreholes of the clay-dominated site. Surface water was additionally collected from a seasonal pond/wetland located in very close proximity to the clay-dominated site and the sample location falls within the same orange star marked for that site. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2.2. *Excitation-emission matrix (EEM) analysis*

Optical analyses were conducted at the British Geological Survey laboratory (Wallingford, UK) following previously described methodology (Lapworth & Kinniburgh, 2009; Tye & Lapworth, 2016; Richards et al., 2019b). Specific ultraviolet absorbance at 254 nm ($SUVA_{254}$) was calculated by division of the absorbance at 254 nm ($A_{254;}$ m^{-1}) by the DOC concentration (mg/L; Weishaar et al., 2003). The EEMs were blank corrected prior to peak-picking and peaks reported in Raman Units (RU). Peak-picking was performed for the EEM values corresponding to tryptophan-like (TPH-like), tyrosine-like (TYR-like), fulvic acid-like (FA-like), humic acid-like (HA-like) fluorescence. Greater values of single-component variables (TPH-like, TYR-like, FA-like and HA-like fluorescence) indicate a greater relative abundance of the compounds they correspond to. The ratio between TPH-like and FA-like fluorescence (TPH:FA-like), was calculated as a proxy for microbially derived over terrestrially derived DOM, which was indicated by greater TPH:FA-like values (Parlanti et al., 2000; Wilson & Xenopoulos, 2009; Richards et al., 2019b). Peak-picking was performed for the calculation of FI (McKnight et al., 2001; Cory et al., 2010), humification index (HIX; Zsolnay et al., 1999), HIX corrected for inner filtration (HIX_{corr}; Ohno, 2002), and “freshness index” (the ratio between relatively freshly produced DOM (microbial-derived or produced in situ, “β”) and more stable DOM (i.e., terrestrial derived carbon compounds, “α”; β:α; Parlanti et al., 2000; Wilson & Xenopoulos, 2009; Kulkarni et al., 2017; Table S1).

2.3. *Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS)*

The samples were shipped frozen to the National High Magnetic Field Laboratory (Tallahassee, Florida, USA) for preparation and analysis. Filtered samples were acidified to pH 2 (10 M HCl) and solid phase extracted (SPE) onto preconditioned Bond Elut 100 mg PPL columns following standard methods (Agilent technologies; Dittmar et al., 2008). The volume of sample extracted was adjusted dependent to the DOC concentration of the sample to achieve a target loading of ~ 40 μg C, assuming an extraction efficiency of 60% (Dittmar et al., 2008). Following extraction, PPL columns were dried with a flow of ultrahigh purity nitrogen gas and eluted with 1 mL of HPLC methanol into pre-combusted (550 °C, 5 h) glass vials and stored at −20 °C until analysis. The eluted samples were analysed using a custom built 21 Tesla FT-ICR MS, using negative-mode electrospray ionization (Hendrickson et al., 2015). Each mass spectrum was formed from 100 scans, conditionally co-added, and subsequently phase corrected (Xian et al., 2010). Spectra were internally calibrated in Predator analysis using the ‘walking’ calibration and 10–15 abundant homologous series that covered each spectra’s molecular weight distribution (Blakney et al., 2011; Savory et al., 2011). Peaks with a signal greater than the root mean square baseline noise plus 6σ were exported to a peak list, and elemental composition assigned between 170–1000 Da using Petroorg© (Corilo, 2014). Assignments of molecular formulae were within the bounds C_{1-100}, H_{4-200}, N_{0-4}, O_{1-30}, and S_{0-2} (error ± 0.3 ppm). Formulae were classed according to elemental stoichiometry (CHO, CHON, CHOS, and CHONS). Double bond equivalent (DBE; an index for the degree of saturation), modified aromaticity index (AI_{mod}; an index for the degree of aromaticity; Koch & Dittmar, 2006; 2016) and NOSC were calculated for assigned formulae, as described elsewhere (LaRowe & van Cappellen, 2011). Carboxylic-rich alicyclic molecules (CRAM-like) compounds were identified by ratios between DBE values and the number of carbon, hydrogen, and oxygen atoms in each formulae. Formulae which fell within the bounds: DBE/C, 0.30–0.68; DBE/H, 0.20–0.95 and DBE/O, 0.77–1.75 were classed as CRAM-like (Hertkorn et al., 2006). Compound class assignments were made based on ratios between C, O, and H, and AI_{mod} values, as follows: condensed aromatics ($AI_{mod} > 0.67$); polyphenolics (AI_{mod} values of 0.5–0.67); highly unsaturated and phenolic compounds (HUPs; $AI_{mod} < 0.5$, $H/C < 1.5$); aliphatics ($H/C \geq 1.5$, $O/C \leq 0.9$ and $N = 0$); peptide-like ($H/C \geq 1.5$, $O/C \leq 0.9$ and $N > 0$); and sugar-like ($H/C \geq 1.5$ and $O/C > 0.9$; Spencer et al., 2014; McDonough et al., 2020). All formulae and compound classes were calculated as percentage relative abundance (%RA; i.e., normalized to intensity of all assigned peaks). The combined concentrations of assigned sugar-like and peptide-like formulae were negligible (<0.3 % RA) and thus not discussed further. Compounds classes were also separated into low O/C ($O/C < 0.5$) and high O/C ($O/C \geq 0.5$) formulae.

2.4. *Data analysis*

The processed EEM and FT-ICR MS datasets, along with the geochemical data (Bassil et al., 2024) were analysed using R (version 3.6.1, included “stats” package). Unpaired Welch *t*-tests were performed, using the “t.test” function, between the groundwater samples taken from the sand- and clay-dominated sites, for all key geochemical, optical and molecular-level DOM metrics that had normal distributions (normality was determined by the Shapiro-Wilk test, where variables that returned p-values < 0.05 were rejected; Table 1).

To identify covariations between geochemical data (As, Fe and DOC concentrations), and optical and molecular-level DOM properties, principal component analysis (PCA) was performed. The optical and molecular parameters selected for PCA were the indices, ratios and % RAs; all single components with absolute measurements (e.g. Abs_{254} and TPH-mean and max) were excluded. These parameters were centred and scaled and the PCAs were performed using the *rda* (redundancy analysis) function within the *vegan* package. The distribution of the parameters (shown by the arrows) was obtained using the *envfit* function. The significance of each parameter was determined by p-values above 0.05, which were also obtained using the *envfit* function. The *stat_elipse* function was used to draw ellipses around the samples grouped by site, at 95% confidence.

Linear regression was performed between Fe and As concentrations, and DOM compositional metrics (e.g., TPH:FA-like fluorescence, HIX_{cor}, and %RA of condensed aromatics and aliphatics) and between optical and molecular-level aromaticity metrics (i.e., $SUVA_{254}$ and AI_{mod}, respectively). Pearson’s correlations were reported for each regression and calculated using the “cor” and “cor.test” functions. The Welch t-tests and the Pearson’s correlations were performed at 95% confidence level, and statistical significance was confirmed when the returned p-values were < 0.05.

3. Results

3.1. *Geochemical and optical DOM properties*

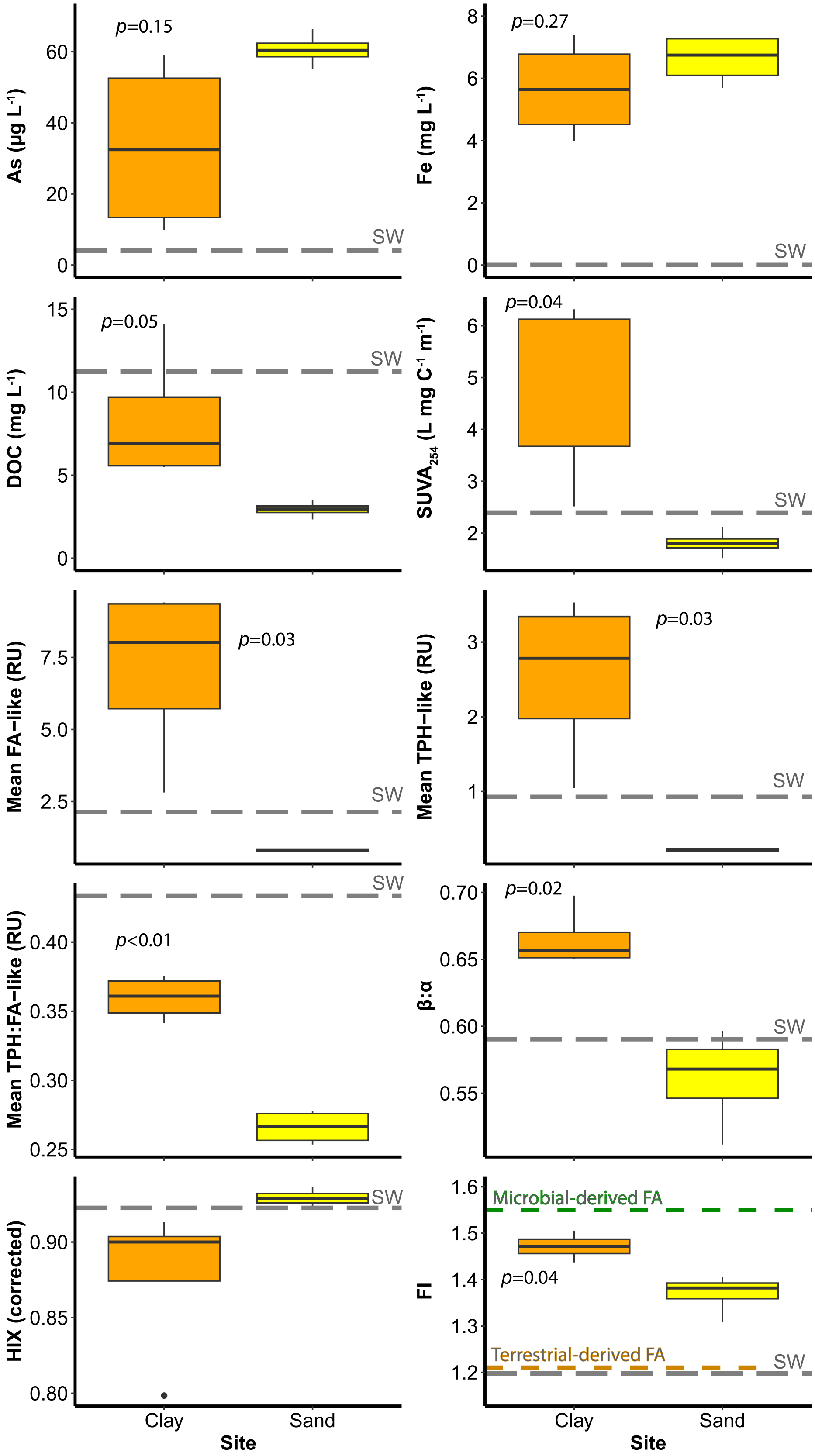
As reported elsewhere, groundwater Fe and As concentrations ranged from 4.0 to 7.4 mg/L and 9.8 to 66 μg/L, respectively (Bassil et al., 2024). Bulk DOC concentrations ranged from 5.5 to 14 mg/L. Higher concentrations of DOC were found in groundwater of the clay-dominated site than the groundwater of the sand-dominated site, with correspondingly lower As concentrations (Table 1 and Fig. 2; Bassil et al., 2024). These values were largely comparable to those of previous studies of the region (e.g., Richards et al., 2019b). Optical metrics showed groundwater DOM was distinct between the clay-dominated and sand-dominated sites and the surface water sample (Table 1 and Fig. 2). The mean $SUVA_{254}$ values were 4.74 (2.52–6.32), 1.81 (1.52–2.12), and 2.40 L mg C^{-1} m^{-1} in the clay-dominated site groundwater, sand-dominated site groundwater, and surface water sample, respectively (Table 1). The single component fluorescence parameters and TPH:FA ratios indicate an overall dominance (terrestrially associated) HA and FA-like fluorescence components over (microbially associated) TPH-like components, in the groundwater and surface water. However, some microbial influence in the groundwater is suggested by the increased FI values in groundwater (1.41–1.51) compared to surface water (1.20) – which compare to end-member values of 1.55 and 1.21

Table 1
Physicochemical and dissolved organic matter (DOM) characteristics of aquifer groundwater and surface water sampled in the Kandal Province, Cambodia, in January 2020. Values are reported as means with ranges given in parentheses.

	Clay-dominated site groundwater mean ($n = 4$)	Sand-dominated site groundwater mean ($n = 4$)	Surface water ($n = 1$)	p value (Welch t-test at 95 % confidence)[b]	Richards et al., (2019b) at 15 m[c]
Water geochemistry [a]					
As (μg/L)	33 (9.8–59)	61 (55–66)	4	>0.05 (0.12)	15–552
Fe (mg/L)	5.7 (4.0–7.4)	6.6 (5.7–7.3)	0	>0.05 (0.33)	0.6–27
DOC (mg/L)[d]	8.4 (5.5–14)	2.9 (2.3–3.5)	11	>0.05 (0.07)	0.9–12
Fluorescence properties (EEM)					
Absorbance					
Abs_{254} (m^{-1})[e]	39.0 (14.1–57.4)	5.24 (4.96–5.50)	26.9	<0.05 (0.04)	
$SUVA_{254}$ (L mg C^{-1} m^{-1})[f]	4.74 (2.52–6.32)	1.18 (1.52–2.12)	2.40	<0.05 (0.05)	~0.0–12.8
TPH-like mean (RU)[g]	2.53 (1.04–3.53)	0.22 (0.20–0.24)	0.93	<0.05 (0.03)	0.25–3.62
TPH-like max (RU)[g]	3.06 (1.26–4.28)	0.28 (0.26–0.29)	1.09	<0.05 (0.03)	
FA-like mean (RU)[h]	7.06 (2.82–9.41)	0.82 (0.77–0.86)	2.14	<0.05 (0.03)	0.85–7.92
FA-like max (RU)[h]	7.47 (3.01–9.99)	0.89 (0.84–0.96)	2.33	<0.05 (0.03)	
HA-like mean (RU)[i]	4.43 (1.67–6.09)	0.58 (0.55–0.63)	1.41	<0.05 (0.03)	
HA-like max (RU)[i]	4.77 (1.79–6.65)	0.63 (0.58–0.67)	1.49	<0.05 (0.03)	
Fluorescence indices					
FI[j]	1.47 (1.44–1.51)	1.31–1.41 (1.37)	1.20	<0.05 (0.01)	1.23–1.55
TPH:FA[k]	0.36 (0.34–0.38)	0.27 (0.25–0.28)	0.43	<0.05 (0.00)	0.27–0.46
HIX[l]	8.12 (3.96–10.5)	13.2 (11.8–14.8)	11.92	<0.05 (0.03)	
HIX (corr)[m]	0.88 (0.80–0.91)	0.93 (0.92–0.94)	0.92	–	0.89–0.95
ß/α[n]	0.67 (0.65–0.70)	0.56 (0.51–0.60)	0.59	<0.05 (0.00)	0.54–0.74
Molecular properties (FT-ICR MS)					
Number of assigned formulae	10,670 (9445–11405)	10,142 (9839–10345)	8473	>0.05 (0.31)	
Average mass (weighted by RA)[o]	554 (544–560)	556 (550–559)	487	>0.05 (0.76)	
Ratios with carbon (weighted by RA)					
O/C	0.47 (0.47–0.48)	0.47 (0.47–0.48)	0.55	>0.05 (0.75)	
N/C	0.01 (0.01–0.01)	0.02 (0.01–0.02)	0.02	<0.05 (0.00)	
H/C	1.15 (1.13–1.17)	1.18 (1.17–1.18)	1.13	–	
Indices (weighted by RA)[o]					
AI_{mod}[s]	0.29 (0.28–0.30)	0.28 (0.27–0.28)	0.28	<0.05 (0.04)	
NOSC[t]	−0.15 (−0.19–-0.13)	−0.18 (−0.19–-0.17)	0.04	–	
Formula classes (%RA)[o]					
CHOS	11.2 (10.4–12.1)	5.5 (5.0–5.8)	11.5	<0.05 (0.00)	
CHONS	1.9 (1.4–2.2)	0.4 (0.3–0.5)	1.9	<0.05 (0.00)	
CHON	23.1 (21.9–24.6)	23.4 (22.7–23.8)	23.0	–	
CHO	63.8 (62.1–65.5)	70.7 (70.5–71.0)	63.6	<0.05 (0.02)	
Compound classes (%RA)[o]					
Aliphatics	3.2 (3.0–3.6)	2.7 (2.7–2.8)	4.6	–	
PPs (low oxygen)[p]	3.9 (3.1–4.8)	2.0 (1.8–2.2)	2.20	<0.05 (0.02)	
PPs (high oxygen)[p]	1.8 (1.2–2.2)	1.5 (1.3–1.7)	5.63	>0.05 (0.21)	
HUPs (low oxygen)[q]	53.0 (51.5–56.7)	55.8 (54.5–56.6)	26.7	–	
HUPs (high oxygen)[q]	37.9 (35.2–40.2)	37.5 (36.8–38.5)	59.4	>0.05 (0.74)	
Condensed aromatics	<0.3	<0.3–0.4	1.2	>0.05 (0.29)	
CRAM-like [o,r]	72.1 (70.5–74.3)	74.4 (73.6–74.9)	52.2	>0.05 (0.06)	

[a] Geochemical values averaged from the technical duplicates of each sample from Bassil et al (2024); [b] p-values calculated by the Welch t-test, to compare the differences between the distributions of the groundwater between the clay- and sand-dominated sites, p-values < 0.05 indicate statistically significant differences at 95 % confidence level, variables marked with a hyphen (–) indicate where samples were not normally distributed and thus Welch t-tests could not be performed; [c] Groundwater EEM values from samples taken at 15 m depth in a previous study of the Kandal Province (Richards et al., 2019b) included for comparison ($SUVA_{254}$ values are averaged across all samples from the previous study); [d] DOC = total dissolved organic carbon; [e] Abs254 = absorbance at 254 nm; [f] $SUVA_{254}$ = specific ultraviolet absorbance (Abs_{254}/DOC); [g] TPH-like = tryptophan-like fluorescence; [h] FA-like = fulvic acid-like fluorescence; [I] HA-like = humic acid-like fluorescence; [j] FI = fluorescence index (McKnight et al., 2001); [k] TPH:FA-like = the ratio between TPH-like and FA-like fluorescence; [l] HIX = humification index (Zsolnay et al., 1999). [m] HIX (corr) = humification index with inner filtration correction (Ohno, 2002); [n]. β:α= "freshness index", the ratio between freshly produced DOM (microbial-derived or produced in situ, "β") and more processed, biostable DOM (i.e., terrestrial derived carbon compounds, "α"; Parlanti et al., 2000; Wilson & Xenopoulos, 2009; Kulkarni et al., 2017). %RA = percentage relative abundance; [p]. PPs = polyphenolics; [q] HUPs = highly unsaturated and phenolic; [r]CRAM-like = carboxyl-rich acyclic-like molecules (Hertkorn et al., 2006); [s].AI_{mod} = modified aromaticity index (Koch & Dittmar, 2006, 2016); [t]. NOSC = nominal oxidation state of carbon (LaRowe & van Cappellen, 2011).

for microbially derived and terrestrially derived fulvic acids, respectively (Cory et al., 2010). The single component parameters (HA-like, FA-like, and TPH-like fluorescence) were higher and more heterogeneous at the clay-dominated site compared to the sand-dominated site (e.g., 2.82–9.41 RU and 0.77–0.86 RU mean FA-like fluorescence respectively; 1.04–3.53 RU and 0.20–0.24 RU mean TPH-like fluorescence respectively; Table 1 and Fig. 2). Indices that were higher in the groundwater DOM of the clay-dominated site compared to that of the sand-dominated included TPH:FA-like ratios (0.34–0.38 vs 0.25–0.28; $p < 0.01$), $SUVA_{254}$ (2.52–6.32 vs 1.52–2.12 L mg/C m^{-1}; $p = 0.05$), FI (1.44–1.51 vs 1.31–1.41; $p = 0.01$), and β:α (0.65–0.70 vs 0.51–0.60; $p < 0.01$; Table 1). On average, HIX_{corr} values were higher at the sand-dominated site compared to clay-dominated, though not statically significant (0.80–0.91 and 0.92–0.94 at clay-dominated and sand-dominated sites, respectively; Fig. 2 and Table 1). The TPH:FA and HIX_{corr} values were higher in the surface water than in the groundwater, whether as the FI values were higher in the groundwater (Fig. 2 and Table 1). The surface water values for $SUVA_{254}$ and β:α were between those of the two groundwater sites Fig. 2 and Table 1).



(caption on next page)

Fig. 2. Key physiochemical and optical properties of the groundwater dissolved organic matter (DOM) sampled from the clay-dominated (Clay) and sand-dominated (Sand) aquifer sites in Kandal Province, Cambodia – sampled in January 2020. Total As and dissolved organic carbon (DOC) were calculated from Bassil et al (2024). Specific ultraviolet absorbance ($SUVA_{254}$; L mg/Cm^{-1}) was calculated from the absorbance at 254 nm divided by the DOC, and is a proxy for aromaticity (Weishaar et al., 2003). FA-like = fulvic acid-like fluorescence. TPH-like = tryptophan-like fluorescence. ß:α = "freshness index", the ratio between recently derived DOM ("β") and more decomposed DOM ("α") (Parlanti et al., 2000; Wilson & Xenopoulos, 2009; Fellman et al., 2010; Kulkarni et al., 2017). HIX_{corr} = humification index with inner filtration correction (Ohno, 2002). FI = fluorescence index, with threshold values for microbial and terrestrial-derived DOM indicated on figure (McKnight et al., 2001). Boxplots show groundwater sites, separated by stratigraphy, and the surface water (SW) sample value is marked by the broken line. The outcome of Welch *t*-test (95% confidence) between the groundwaters of the clay-dominated and sand-dominated sites is indicated by the p-values; significance is indicated when $p < 0.05$ (this could not be performed on the HIX_{corr} due to non-normal distribution).

3.2. *Molecular-level DOM properties*

Between 9,445 and 11,405 molecular formulae were assigned in the groundwater of the clay-dominated site, 9,839 to 10,345 molecular formulae in the groundwater of the sand-dominated site, and 8,473 molecular formulae in the surface water (Table 1), which may indicate higher molecular diversity in the groundwaters than in the surface water sample. The groundwater of the sand-dominated site had slightly higher H/C ratios (1.17–1.18) than the groundwater of the clay-dominated site (1.13–1.17; Table 1). The surface water had a lower H/C ratio (1.13) and higher O/C ratio (0.55) than the groundwaters (0.47–0.48; Table 1). Higher AI_{mod} values were found in the groundwater of the clay-dominated site (0.28–0.30) than in the groundwater of the sand-dominated site (0.27–0.28), and the surface value (0.28) was between those of the groundwater sites (Table 1 and Fig. 3). Overall NOSC values were negative in the groundwater (−0.19 to −0.13) and slightly positive in the surface water (0.04; Table 1 and Fig. 3).

The most abundant formulae class was CHO (61.2–70.7 %RA in the groundwater, 63.6 %RA in the surface water), followed by CHON, CHOS and CHONS (Fig. 4A). The groundwater of the clay-dominated site and the surface water contained higher %RA of sulfur-containing formulae (CHOS, CHONS) than the groundwater of the sand-dominated site (10.4–12.1 %RA in surface water and clay-dominated site groundwater compared to 5.0–5.8 %RA in sand-dominated site groundwater; Table 1 and Fig. 4A). HUP compounds dominated the molecular-level composition of all samples (90.1–93.6 %RA in the groundwater, 86.1 %RA in the surface water), polyphenolics were the second most abundant compound class (3.3–6.9 %RA in the groundwater, 7.8 %RA in the surface water), followed by aliphatics (2.7–3.6 %RA in the groundwater, 4.6 %RA in the surface water) and condensed aromatics (<0.3–0.4 %RA in the groundwater, 1.2 %RA in the surface water; Table 1 and Fig. 4B). HUP and polyphenolic compounds in groundwater samples were dominated by low O/C ratios (<0.5, e.g. 51.5–56.6 %RA low oxygen HUPs; Table 1), whilst those in the surface water sample predominantly had high O/C ratios (0.5 or higher; e.g. 59.4 %RA HUPs; Table 1 and Fig. 4B). The groundwater also had significantly higher CRAM-like formulae (70.5–74.9 %RA) compared to the surface water (52.9 %RA; Fig. 3 and Table 1).

3.3. *Covariations between geochemical, optical and molecular characteristics*

Strong positive correlations were found between $SUVA_{254}$ and AI_{mod} ($r = 0.97$; Fig. 5) as well as strong negative correlations between the $SUVA_{254}$ and CRAM-like relative abundances, though only for the groundwater samples ($p < 0.01$; Fig. 5).

Overall, optical and molecular analysis showed a dominance of terrestrially derived DOM in both clay- and sand-dominated sites (Figs. 2–4), although comparison of FI values indicate that the fulvic acids in the groundwater had a substantial microbial influence (Fig. 2). However, DOM composition differed between groundwaters, particularly clay-dominated groundwater had a higher freshness index and % RA of aliphatic compounds compared to sand-dominated groundwater. In order to understand what drives this variability, and identify relationships between DOM composition and As release, a principal component analysis was conducted (PCA). Two PCAs were performed given the substantial differences in composition between the surface water and groundwater (Figs. 2 and 3). The first PCA was conducted on all the samples collected (i.e., the groundwater and surface water samples; Fig. 6A) to identify the covariations in DOM composition and As concentrations between surface and groundwaters. The second PCA was performed on the groundwater samples only (Fig. 6B), in order to identify the differences between (and co-variations within) the clay-dominated and sand-dominated sites.

When the surface water sample is included, the clay-dominated site groundwater and surface water was differentiated from the sand-dominated site groundwater by PC1 (48.9% of total variance), whilst the surface water is differentiated from the clay-dominated site groundwater by PC2 (31.6% of total variance; Fig. 6A). The surface water sample is characterised by higher NOSC values, and an increased %RA of condensed aromatics and aliphatics, as well as a high O/C polyphenolics and high O/C HUP compounds (Fig. 6A). Fe and As concentrations were associated with positive values on PC1, and thus DOM with relatively higher low O/C HUP and CHO-only compounds, when all samples are included (Fig. 6A).

The PCA performed solely on the groundwater samples also showed differentiation by site along PC1 (56.5% of total variance), with those of

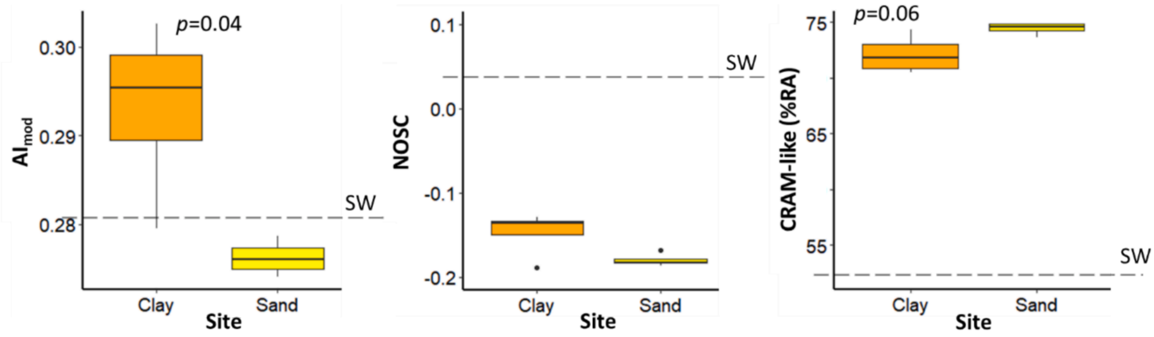


Fig. 3. Modified aromaticity index (AI_{mod}), nominal oxidation state of carbon (NOSC), and the relative abundances (%RA) of carboxyl-rich acyclic molecules (CRAM-like), in the aquifer groundwaters of the clay-dominated (Clay) and sand-dominated (Sand) sites ($n = 4$ at each site) and a single surface water sample (SW; $n = 1$) in the Kandal Province, Cambodia. The outcome of Welch *t*-test (95% confidence) between the groundwaters of the clay-dominated and sand-dominated sites is indicated by the *p*-values, significance is indicated when $p < 0.05$ (this could not be determined on NOSC values due to non-normal distributions).

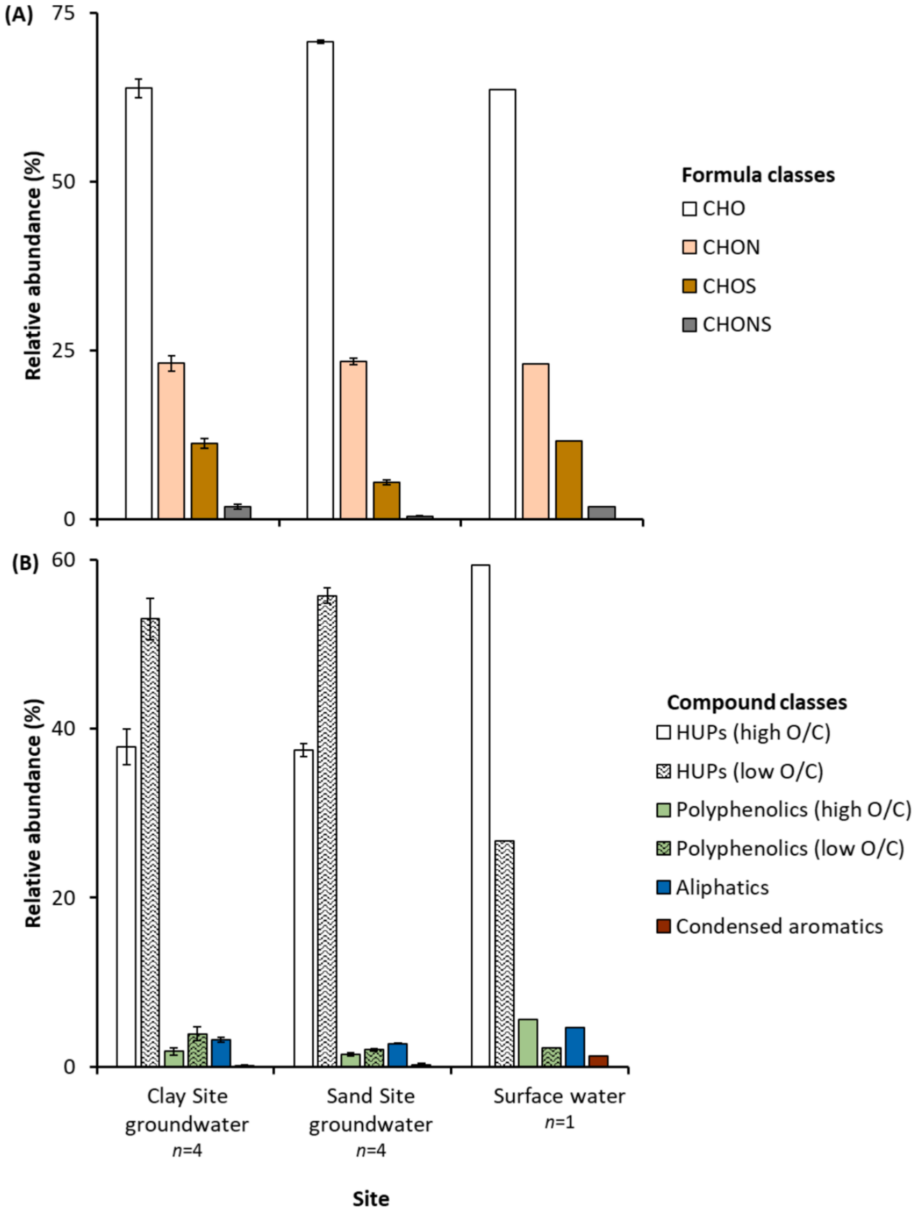


Fig. 4. Heteroatom classes (A) and compound classes (B) by relative abundance (RA) within the groundwaters of the clay-dominated (Clay; $n = 4$) and sand-dominated (Sand; $n = 4$) boreholes and the surface water sample ($n = 1$). HUPs = highly unsaturated and phenolic compounds. Low O/C = <0.5; high O/C $\geq$ 0.5.

the clay-dominated site on the negative side, and those of the sand-dominated site on the positive side (Fig. 6B). Furthermore, the groundwater-only PCA showed separation by TPH:FA-like fluorescence, β:α, FI, as well as %RA of sulfur-containing formulae (CHOS, CHONS), polyphenolics, O/C HUPs, aliphatics, and NOSC values (weighted by RA) on the negative side of PC1; and higher Fe concentrations, As concentrations, %RA of CRAMs, low O/C HUPs, CHO formulae on the positive side of PC1. PC2 (23.9% of total variance), which appeared to be driven by variables related to aromaticity (e.g., $SUVA_{254}$ and polyphenolics on the negative side of PC2, and low oxygen HUPs on the positive side of PC2; Fig. 6B). There was no clear site-separation along PC2, however there was wider variation in the clay-dominated site samples compared to the sand-dominated site samples along PC2 (Fig. 6B). Along PC1, higher Fe and As concentrations are weakly associated with the sand-dominated site groundwater (i.e., Welch t-tests show As concentrations are statistically similar between the groundwaters of the clay-dominated and sand-dominated sites; Table 1). Higher DOC concentrations appeared to be associated with the clay-dominated site groundwater (Fig. 6B), although this association is not statistically significant according to the Welch t-tests between the sites ($p = 0.07$; Table 1). Furthermore, in both PCAs, high O/C HUPs, condensed aromatics, and HIX_{corr} had *envfit* *p*-values of > 0.05 (Fig. 6 and Box S1), indicating that these variables did not significantly contribute to overall variation, though may still be important with respect to the sites they are distributed with.

4. Discussion

4.1. DOM sources and microbial processing

The $SUVA_{254}$ values were comparable to waters of As-prone aquifers elsewhere, such as in the Hetao Basin (1.43 to 2.09 L mg C^{-1} m^{-1} surface water, 1.33 to 7.35 L mg C^{-1} m^{-1} in groundwater; Qiao et al., 2021) the Bengal Basin (2.48 to 3.23 L mg C^{-1} m^{-1} in surface water, 0.40 to 4.65 L mg C^{-1} m^{-1} in groundwater; Kulkarni et al., 2017), Datong Basin (0.72 L mg C^{-1} m^{-1} in surface water, 0.18 to 0.62 L mg C^{-1} m^{-1} in groundwater;

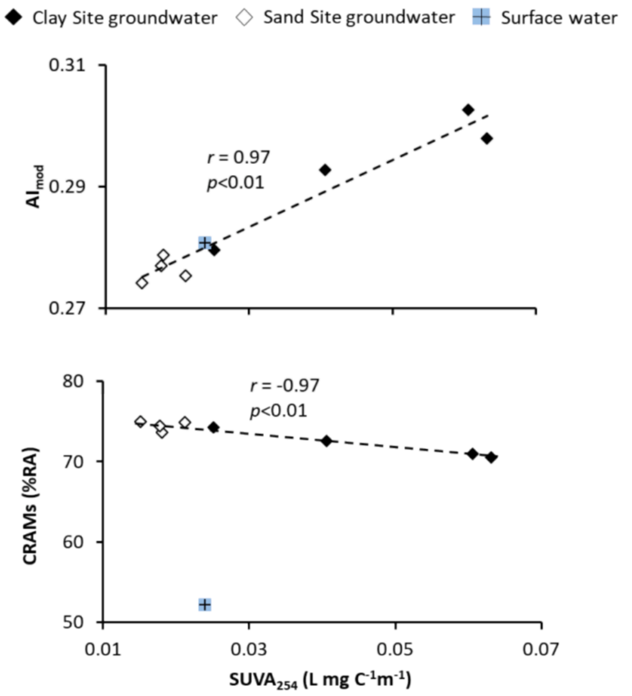


Fig. 5. Pearson's correlations between specific ultraviolet absorbance at 254 nm ($SUVA_{254}$), and modified aromaticity index (AI_{mod}; top) and relative abundance (%RA) of carboxyl-rich alicyclic-like molecules (CRAM-like; bottom). Line of best fit and r values are for groundwater samples only. Clay GW = groundwater samples from the clay-dominated site ($n = 4$). Sand GW = groundwater samples from the sand-dominated site ($n = 4$).

Pi et al., 2015) and the Indus Delta (0 to 8.1 L mg C^{-1} m^{-1} in groundwater; Malik et al., 2020). Although dissolved Fe is known to increase absorbance at 254 nm (Poulin et al., 2014) and thus influence $SUVA_{254}$ values, a previous study on groundwaters from these Cambodian field sites compared shaken to unshaken samples to assess the potential impact of Fe oxyhydroxide particulates in the samples (brought into suspension by shaking) and found no significant difference in Abs_{254} readings (Richards et al., 2019b). In addition, in this study, no correlation was found between Fe concentrations and $SUVA_{254}$ values in the groundwater samples (Supplementary Fig. S2). Furthermore, the strong positive correlations between groundwater $SUVA_{254}$ values with independent molecular-level metrics of aromaticity AI_{mod} ($r = 0.97$; Fig. 5), is in agreement with the use of $SUVA_{254}$ as a proxy for aromaticity (Weishaar et al., 2003).

The higher heterogeneity of (optical and molecular) DOM signatures in the clay-dominated sites, compared to that of the sand-dominated site, is likely due to the lower recharge rates and lower connectivity between the wells in clay-dominated lithology (Uhlemann et al., 2017; Richards et al., 2017 and 2019b). The overall optical characteristics with respect to the groundwaters of the clay-dominated and sand-dominated sites (Fig. 2), were also very similar to those of previous studies in the Kandal Province, and the domination of humic and fulvic acid-like fluorescence over that of tryptophan-derived (associated with microbially-derived DOM) were consistent with the importance of surface-derived terrestrial organics on groundwater hydro-geochemistry (Richards et al., 2019b). At the molecular-level, the presence of polyphenolics in the groundwater was also in line with terrestrial, surface derived organics from plant-material into the groundwater (Hättenschwiler & Vitousek, 2000). The higher abundance of polyphenolics in the clay-dominated site groundwater compared to the sand-dominated site groundwater (Fig. 4) is also consistent with associations between clay-dominated aquifer sediments and plant-derived material, observed in previous studies of aquifers in Cambodia (Rowland et al., 2007; van Dongen et al., 2008; Magnone et al., 2017) and northern Vietnam (Al Lawati et al., 2012; Glodowska et al., 2020). This may indicate build-up of surface/plant-derived compounds in the clay-dominated aquifers and/or the preservation of plant-derived material in the clay-dominated sediments or pores, and mobilisation into the groundwater.

The similarity in %RA of sulfur-containing formulae (CHON and CHOS) between the surface sample and the clay-dominated site groundwater (Fig. 4A) possibly reflects the close proximity of the lake (where the surface water sample was taken) to the boreholes of the clay-dominated site. The lower O/C ratios, NOSC values, and higher H/C ratios and %RA of CRAM-like molecules in groundwater (from both sites) compared to surface water (Figs. 3 and 4), are likely explained by biodegradation and are broadly consistent with that of unconfined aquifers < 41 m depth, in a recently proposed framework for DOM cycling in groundwater (McDonough et al., 2022). Under this framework, aromatic DOM from the surface percolates into aquifers and biodegradation leads to a removal of compounds with a higher NOSC. This results in a decrease in O/C ratios and an increase in H/C ratios, as well as an increased %RA of CRAM-like molecules down flow path (McDonough et al., 2022). The removal of these higher NOSC compounds during microbial degradation in the subsurface is consistent with OM-degradation studies of As-prone aquifer sediments from Bangladesh and the Hetao Basin, which have shown mean %RA weighted NOSC decrease during bioincubation, as compounds with a higher NOSC preferentially metabolized (Pracht et al., 2018; Qiao et al., 2020). A study in the As-prone Jianghan Plain, suggested that organic compounds with CRAM-like molecular formulae may also be reused in biogeochemical processes (including As release; Yu et al., 2020). However, there is no clear evidence for the reuse of CRAM-like molecular formulae as electron donors in this study, although this cannot be completely excluded given the high %RA of CRAM-like molecular formulae in the groundwater compared to the surface (Fig. 3). Therefore, the differences in DOM molecular composition between the surface and groundwater observed in this study, particularly NOSC values, and in the relative abundance of high O/C formulae, CRAM-like molecular formulae (Fig. 6A), may reflect the microbial processing of DOM that has occurred since percolation from the surface into the aquifer. This microbial processing may also explain the microbial influence in groundwater DOM suggested by the FI values observed (Fig. 2; Cory et al., 2010). Previous studies in the Kandal Province have shown groundwater DOC age at 15 m (i.e., the depth of sampling in this study) to be ~ 5960 years BP in the clay-dominated area (LR12–LR14 in Fig. 1; near the clay-dominated site boreholes in this study), and ~ 1240 years BP near the sand-dominated area (LR01 in Fig. 1; near the sand-dominated site boreholes in this study; Magnone et al., 2019). Radiocarbon dating of DOC from previous studies at these sites combined with the molecular-level composition of DOM observed here indicate that the microbial processing of DOM may occur during these time-periods, even at the relatively shallow depth of 15 m. However, the differences in residence time between the clay-dominated site and sand-dominated site groundwaters (Magnone et al., 2019) did not appear to have exerted a significant effect on the %RA of aliphatics and heteroatom (N and S) containing formulae (Table 1), which are thought to accumulate in anoxic groundwater (such as the groundwaters in this study), due to the lack of degradation (McDonough et al., 2022).

Additionally, SOM may be an important DOM source and thus may influence the compositions observed here. Previous studies in the area have shown that inorganic carbon derived from oxidation of DOC predated modelled groundwater flow by hundreds of years, and thus SOM derived compounds may drive As release, opposed to surface-derived sources (Magnone et al., 2017, 2019). The importance of SOM has further been highlighted in previous microcosm studies, which indicated microbial Fe(III)/As(V) reduction and As release where SOM was used as electron donor, including petroleum-derived compounds (Rowland et al., 2007, 2009). The detection of petroleum-derived compounds in

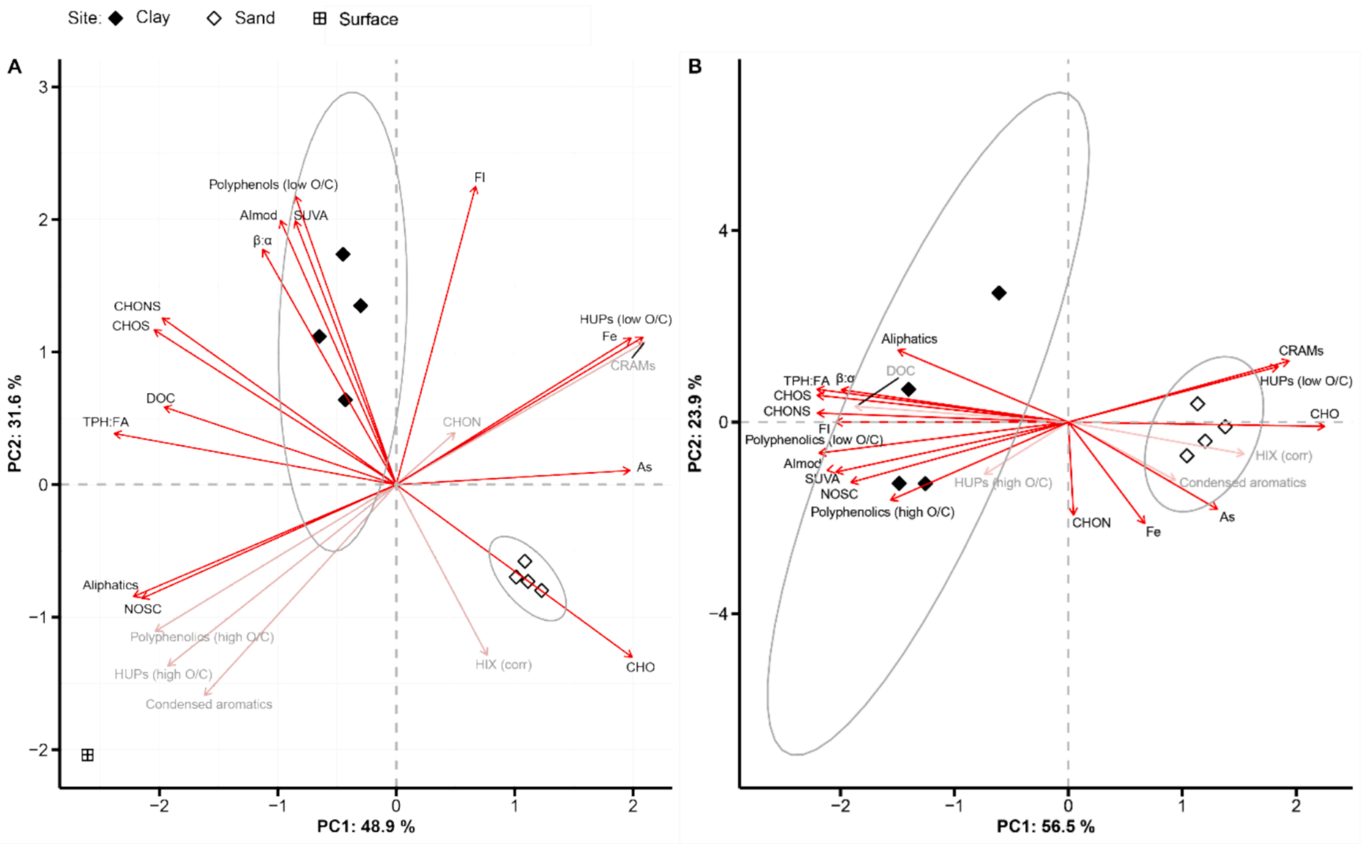


Fig. 6. Principal component analysis (PCA) of Fe, As and dissolved organic carbon (DOC) concentrations, along with optical and FT-ICR MS metrics. (A) Groundwater and surface water samples. (B) Groundwater samples only. Red circles show close parameter co-variations; blue circles show the respective plots locations of the clay-dominated site (negative side of PC1 in both PCAs) and sand-dominated site (positive side of PC1 in both PCAs) groundwater samples, and the surface water sample (negative side of PC1 and PC2 in first PCA). $SUVA_{254}$ = specific ultraviolet absorbance at 254 nm (Abs_{254}/DOC). TPH:FA-like = the ratio between tryptophan-like and fulvic acid-like fluorescence. HIX_{corr} = humification index with inner filtration correction (Ohno, 2002). ß:α = "freshness index", the ratio between recently derived DOM ("β") and more decomposed DOM ("α") (Parlanti et al., 2000; Wilson & Xenopoulos, 2009; Fellman et al., 2010; Kulkarni et al., 2017). HUPs = highly unsaturated and phenolic compounds. AI_{mod} = modified aromaticity index (Koch & Dittmar, 2006, 2016). NOSC = nominal oxidation state of carbon (LaRowe & van Cappellen, 2011). Clay GW = groundwater samples from the clay-dominated site (n = 4). Sand GW = groundwater samples from the sand-dominated site (n = 4). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

FT-ICR MS data is possible, but challenging to identify when DOM composition has multiple sources. It is possible that some organic compounds (derived from co-deposition or upwelling) could have been sorbed onto the sediment grains (Bauer & Blodau, 2006). It is also possible that some (higher NOSC) terrestrial-derived DOM compounds could have been sorbed onto aquifer sediments down the flow path, which has been suggested to occur in shallow aquifers (McDonough et al., 2022). In the event of any sorption of organic compounds onto the sediments, they would not appear in the DOM pool, and it is possible that any degradation/oxidation occurred whilst bound to the sediments.

Sulfur-containing formulae (CHOS and CHONS) were the lowest in %RA of all the formula classes (e.g., CHOS formulae 5.0 to 12.1 %RA; Table 1). This contrasts with that previously measured in the recharge waters and sediment porewaters of Bangladesh (47.3 to 58.9 %RA; Pracht et al., 2018) and is also marginally lower than values previously measured in aquifer waters of the Hetao Basin (7.0 to 16.0 %RA in groundwaters, 16.6 to 23.3 %RA in surface waters; calculated from Qiao et al., 2021). The relatively lower abundance of sulfur-containing formulae noted in this study is likely a reflection of the lower amounts of sulfur in the Kandal Province groundwaters (Richards et al., 2017), highlighting that sulfur species may not play a major role in the DOM cycling at these sites.

Nonetheless, the association between sulfur-containing formulae and tryptophan-like fluorescence found here may indicate biodegradation and the accumulation of S-containing organics, further indicating the importance of microbial processes in forming the DOM compositions observed at these sites (Fig. 6). This association has also been previously noted in the Hetao Basin groundwaters (Qiao et al., 2021), where microbial sulfate reduction and the production of sulfides allows for abiotic sorption or incorporation of S- into DOM (Qiao et al., 2021 and references therein). Furthermore, Pracht et al. (2018) showed an increase in organic sulfur compounds during incubation of aquifer material from Bangladesh. At these sites in the Kandal Province, sulfate-reducing conditions have previously been noted from modelling of mineral saturation, for instances supersaturation of pyrite, orpiment and realgar were observed at 6 and 9 m depth at near the sand-dominated site of this study (LR01), and 21 m depth near the clay-dominated site of this study (LR14; Fig. 1) but not at 15 m depth (at which the groundwater samples in this study were taken; Richards et al., 2017). Sulfur-containing formulae may suggest microbial processing of DOM (Spencer et al., 2019; Behnke et al., 2021; Vaughn et al., 2021). Furthermore, in the McDonough et al (2022) framework, heteroatom-containing formulae (i.e., N or S containing species) are thought to accumulate during biodegradation under suboxic or anoxic conditions and may also increase in abundance due to hydrogenation on unsaturated formulae and sulfurization (aided by sulfate reduction). As such, the higher %RA of CHOS and CHONS formulae at the clay-dominated site groundwater, than that of the sand-dominated groundwater (Table 1) might therefore suggest greater microbial cycling than that at the sand-dominated site, either through sulfate reduction or microbial cycling of the organic matter (Wagner et al., 2015; Yuan et al., 2017). However, high abundances of S-containing formulae were also found in the (oxic) surface water (Table 1) which might suggest microbial production of S-containing compounds (McDonough et al., 2022), especially since %RA of aliphatics were higher in the surface water compared to that of the groundwater (4.6 %RA in surface water, compared to 2.7 to 2.6 %RA in the groundwater; Table 1). Incubations studies would be needed to further understand the impact of microbial degradation on the DOM at these aquifers and the relation to Fe, As and sulfur cycles thereof.

4.2. DOM composition and association to as release

Positive Pearson's correlations were found between groundwater As concentrations and indicators of terrestrially derived OM and some indicators of relatively biostable DOM (e.g., HIX_{corr} values; $r = 0.73$; $p = 0.039$; Supplementary Fig. S1). This is in line with DOM analysis of relatively shallow (<40 m depth) groundwater in the Hetao Basin that indicated positive correlations between As concentrations and %RA of biostable compounds (e.g., humics; Qiao et al., 2020, 2021; Wang et al., 2023). These observations are further supported by negative correlations between groundwater As concentrations and optical properties, such as TPH:FA-like fluorescence ($r = –0.78$; $p = 0.023$; Richards et al., 2019b; Qiao et al., 2020, 2021), as well as %RA of aliphatics ($r = –0.82$; $p = 0.013$). Here, similar associations were observed between groundwater Fe concentrations and the aforementioned metrics (e.g., TPH:FA ratio and %RA of aliphatics), although these were not statistically significant ($p > 0.05$; Supplementary Fig. S1). However, statistically significant positive Pearson's correlations did occur between groundwater Fe concentrations and abundances of condensed aromatics ($r = 0.74$; $p = 0.038$), but not As concentrations ($r = 0.49$; $p = 0.213$; Supplementary Fig. S1).

The negative associations between TPH:FA ratios and %RA of aliphatics with As and Fe concentrations (Fig. 6) may suggest the degradation of biolabile DOM in connection of Fe(III)/As(V) reduction and As release, and possibly the utilisation of stable compounds (e.g., humics) as electron shuttles in Fe(III)/As(V) reduction (Qiao et al., 2020, 2021). The differences in Fe and As distributions in relation to organic variations (Supplementary Fig. S1 and Table S2) could be related to the different sorption behaviours of these elements to organic compounds and mineral surfaces. Although no data on the SOM characteristics and biodegradability is available from the boreholes used in this study, comparative molecular studies between (water-extractable) SOM and groundwater DOM in other regions indicated a relative higher biolability for the SOM (Qiao et al., 2020). It is therefore likely that SOM could have acted as electron donors in Fe(III) and/or As(V) reduction and As release with the more stable end-products released into the groundwater DOM. No statistically significant correlations occurred between either Fe or As concentrations and ß:α (vs Fe, $p = 0.373$; vs As, $p = 0.064$) and NOSC (vs Fe, $p = 0.628$; vs As, $p = 0.876$; Supplementary Table S2), although typically higher NOSC and ß:α values were associated with lower As concentrations (Fig. 6). This likely reflects the complexity in groundwater flow and the respective sources of Fe, As and organic compounds present in the Kandal Province aquifers (Lawson et al., 2013, 2016; Richards et al., 2017, 2018; Magnone et al., 2019), highlighting that more spatial and temporal (e.g., pre and post monsoon) analyses would be needed to substantiate the relationship between DOM composition and As and Fe release. Furthermore, the trends identified in this study and studies of shallow groundwaters (<40 m) of the Hetao Basin (Qiao et al., 2020, 2021; Wang et al., 2023) somewhat contrast with studies of deeper groundwaters (>40 m) in the Songen and Hetao Basins (>40 m), which have identified positive relationships between DOM biodegradability and As concentrations in some studied aquifers (Gao et al., 2023; Li et al., 2024). These results highlight the need to include multiple depths of sampling as well as spatial variation in future studies.

Overall, the present study indicates that the combined use of FT-ICR MS and optical analyses can yield valuable information about the composition of groundwater DOM in As-prone aquifers, and the relation thereof with As-release from sediments. However, larger sample sizes taken across wider transects (combined with models of groundwater flow) and incubation experiments on the samples, would be needed to confirm and decipher any potential trends between groundwater As and the molecular characteristics of groundwater DOM, along hydrogeological flow paths. Future studies would therefore benefit from application of FT-ICR MS alongside optical characterisation on As-prone aquifers, along groundwater flow transects at multiple depths with contrasting hydrogeochemical characteristics (e.g., As concentrations and methane release), to further understand the relationship between As release and carbon cycling in aquifers. High spatial and temporal resolution is possible through optical measurements due to low costs and sample volumes required (Kulkarni et al., 2017; Richards et al., 2019b), whilst FT-ICR MS provides unparalleled resolution (Spencer et al., 2014, 2015; Derrien et al., 2019; McDonough et al., 2022) – the combined use of both methods therefore can provide "*the best of both worlds*". Future studies should also include incubation experiments to directly measure groundwater DOM biolability in conjunction with molecular composition to robustly connect DOM composition and biolability to Fe, As (and sulfur) cycling in the environment. Such experiments could allow cross-referencing of changes in biogeochemical processes (i.e. DOM composition and As release) with microbial communities and functions. A detailed understanding of these processes at molecular-level would significantly aid the prediction of As cycling in vulnerable aquifers and therefore help improve groundwater management practices.

5. Conclusion

This study aimed to provide insights into the environmental sources and processing of groundwater DOM, and its role in As release in the aquifers of Kandal Province, Cambodia, by analysis and comparison between novel molecular and optical properties with geochemical data. Fluorescence indices suggest overall dominance of terrestrially derived DOM in groundwaters in both the clay-dominated and sand-dominated aquifer sites (although a degree of microbial processing is suggested by the FI values), and potentially higher biodegradability in the groundwaters of the clay-dominated site. Fluorescence indices for aromaticity were validated by comparison to the molecular data and fluorescence indices for microbial-sources (e.g., high FI and high TPH:FA ratio) co-varied with sulfur-containing formulae suggesting microbial processing of DOM. The combined molecular and fluorescence analyses shows that groundwater DOM in the shallow aquifers is influenced by a variety of sources (including terrestrial/surface-derived compounds, e.g., polyphenolics), which in turn may be influenced by subsurface microbial processing (suggested by high CRAM-like abundances and low NOSC values in groundwaters compared to surface). Negative correlations between dissolved As and Fe with TPH:FA and %RA of aliphatic compounds likely indicate degradation of biolabile compounds and accumulation of stable compounds, in connection with As release. This is consistent with the role of biolabile organic compounds as electron donors in As release, by reductive dissolution as well as possible electron shuttles at both sites. Together, these findings highlight the role DOM composition plays in microbially mediated As release.

CRediT authorship contribution statement

Oliver C. Moore: Lead researcher, conducted the fieldwork, performed the data analysis and data display, wrote the manuscript.. **Amy D. Holt:** Writing – review & editing, Methodology, Formal analysis, Data curation. **Laura A. Richards:** Writing – review & editing, Supervision, Investigation, Conceptualization. **Amy M. McKenna:** Writing – review & editing, Methodology, Formal analysis, Data curation. **Robert G.M. Spencer:** Writing – review & editing, Validation, Methodology, Formal analysis, Data curation. **Dan J. Lapworth:** Writing – review &

editing, Methodology, Formal analysis, Data curation. **David A. Polya:** Writing – review & editing, Supervision, Conceptualization. **Jonathan R. Lloyd:** Writing – review & editing, Supervision, Project administration, Funding acquisition. **Bart E. van Dongen:** Writing – review & editing, Visualization, Supervision, Project administration, Methodology, Investigation, Conceptualization.

Funding

This work was funded by NERC through a PhD studentship of the Manchester-Liverpool Earth Atmosphere and Ocean Doctoral Training Program (EAO DTP; NE/L002469/1) and supported by the NERC-funded GOAM project (NE/P01304X/1). Dan Lapworth was supported by the BGS International NC programme 'Geoscience to tackle Global Environmental Challenges'. LAR acknowledges a Dame Kathleen Ollerenshaw Fellowship and a NERC Exploring the Frontiers Award (NE/X010813/1). The molecular characterisation portion of this work was performed at the National High Magnetic Field Laboratory ICR User Facility, which is supported by the National Science Foundation Division of Chemistry and Division of Materials Research through DMR-2128556 and the State of Florida.

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.

Acknowledgements

We would like to thank Chivuth Kong, Pheaktra Sovann, all other staff at the Royal University of Phnom Penh and the Resource Development International Cambodia (RDIC), as well as all drivers and borehole drillers, who helped facilitate the fieldwork. We also thank Naji Bassil for his assistance in the fieldwork. We would also like to thank Daren Gooddy and Peter Williams for their assistance in facilitating the EEM analysis at BGS, Wallingford, UK. Dan Lapworth publishes with the permission of the Executive Director of the British Geological Survey. We thank the anonymous reviewers for their feedback, which has contributed to the improvement of this manuscript.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.orggeochem.2024.104886.

Data availability

Data will be made available on request.

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