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RESEARCH ARTICLE

Fluorescence spectroscopy reveals accompanying occurrence of ammonium with fulvic acid-like organic matter in a fluvio-lacustrine aquifer of Jianhan Plain

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Abstract This study is the first to investigate the simultaneous presence of NH_4^+ and fluorescent organic matter components (FOCs) from a fluvio-lacustrine aquifer in Central Jianghan Plain. Sediment, groundwater, and surface water samples were collected for the sediment organic matter extraction, 3D fluorescence spectroscopy characterization, and/or hydrochemical analysis. NH_4^+ and dissolved organic carbon was ubiquitous in the groundwater. The fluorescence spectroscopy revealed good relationships between NH_4^+ and fulvic acid-like components (FALCs) in the groundwater and sediment-extracted organic matter (SEOM) solutions. NH_4^+ also exhibited significant positive correlation with protein-like component (PLC) ($p < 0.001$), with the stronger in the SEOM solutions than that in groundwater. Comparisons of spectroscopic indices [e.g., humification index (HIX), biological index (BIX), spectra slope ($S_{275–295}$), and specific UV absorbance ($SUVA_{254}$)] between the groundwater and SEOM solutions revealed more labile properties of SEOM. This result indicates that the decreasing NH_4^+–FOCs correlations of groundwater relative to sediments may be attributed to microbial degradation. Factor analysis identifies important factors that cause NH_4^+ occurrence in the groundwater. The accompanying increase of FALC (C1) and NH4–N with the mole concentration of the normalized $HCO_3^-/(Ca^{2+}+Mg^{2+})$ and $[H^+]$ suggests that couple effects of various biodegradations simultaneously occur in the aquifer, promoting the occurrence of NH_4–DOMs.

Keywords NH_4^+ · Groundwater · DOM · 3D fluorescence spectroscopy · Hydrochemistry · Factor analysis

Introduction

Nitrogen speciation in the environment plays key roles in maintaining life activity and regulating the nitrogen balance in the ecosystem. NO_3^- and NH_4^+ are the two most important forms of reactive nitrogen and the main nitrogen species of concern. Groundwater NO_3^- has been extensively investigated worldwide (Hinkle and Tesoriero 2014; Spalding and Exner 1993); however, groundwater NH_4^+ has received relatively less research attention. Despite having no direct risk to human health, a high concentration of NH_4^+ can potentially increase NO_3^- concentration via nitrification (Umezawa et al. 2008), which in turn leads to eutrophication of recharged surface water. In special conditions, groundwater NH_4^+ can indicate the presence of hazardous contaminants, such as

pathogens and pesticides (Umezawa et al. 2008). Therefore, ammonium is regulated as a contaminant in several countries, including the UK and China; both countries prescribe a 0.5 mg/L maximum limit concentration of ammonium in drinking water (PRC Ministry of Health and Standardization Administration 2006; Erskine 2000).

NH_4^+ indicates the reducing condition of groundwater, and its occurrence has been commonly identified to be attributed to the denitrification of infiltrated NO_3^- (anthropogenic source) (Stumm and Morgan 1996). Recently, the natural occurrence of NH_4–N in aquifers, which may be easily overlooked, has been increasingly documented. Jiao et al. (2010) found abnormally high levels of NH_4^+ in the coastal aquifer system of the Pearl River Delta. Their study suggests that NH_4^+ is related to the high content of organic nitrogen in organic matter (OM)-rich aquitards. NH_4^+ is also identified as one of the main nutrients that are released from sedimentary organic matter (SOM) through submarine groundwater discharge processes (Gleeson et al. 2013; Santos et al. 2008). Most of the relevant observations are from coastal aquifers (Manning and Hutcheon 2004). Few studies have suggested the natural occurrence of ammonium in fresh groundwater (Glessner and Roy 2009; Hinkle and Tesoriero 2014). However, the detailed OM source information has not been specifically examined, especially the associations of NH_4^+ with OM components between sediments and groundwater.

Jianhan Plain is a large-scale river basin in Central China that is formed by the Yangtze and Han rivers (Duan et al. 2015; Huang et al. 2013). Widespread lacustrine sediments with abundant OM are observed in the low-flat part of the plain in the middle reaches of the Yangtze River (Huang et al. 2013). Previous studies showed the reducing quality of groundwater in the study area as evidenced by the reductive hydrochemical indices. Significant levels of NH_4^+, bicarbonate, and dissolved organic carbon (DOC) were ubiquitous in the groundwater. Given the relatively closed nature of the aquifer and the prevalence of NH_4^+ and DOC, we inferred that observed anthropogenic point sources (typically shallow or surface NO_3^-) unlikely cause the widespread NH_4^+ in groundwater. Therefore, we hypothesize that the occurrence of NH_4^+ may be linked to the OM of aquifers.

Given that the presence of NH_4^+ in groundwater may be related to OM source, the relationships between NH_4^+ and specific OM components should be determined. 3D fluorescence spectroscopy is a simple and convenient method that can provide a considerable amount of information on the composition and structure of DOM (Hur and Kim 2009; Wang et al. 2014). This method is highly sensitive at natural abundance levels and has been widely used to assess the quality of DOM in various aquatic systems (Fellman et al. 2010). By using this method, we report the concurrence of NH_4^+ and fluorescent OM components (FOCs) in the groundwater of a fluvio-lacustrine aquifer in Jianghan Plain, where widespread occurrence of DOC was

believed to influence its groundwater chemistry significantly (Huang et al. 2015; Huang et al. 2012). The presented relationships of specific FOC with NH_4^+ and characteristic hydrochemical parameters provide new insights into the NH_4^+ genesis in an OM-rich lacustrine aquifer. Our approach for determining the occurrence of NH_4^+ in groundwater may be applicable to other regions that have similar conditions.

Materials and methods

Study area and sample collection

The study was conducted in the town of ShaHu in the Central Jianhan Plain (30° 08′ N, 113° 40′ E) (Fig. 1) where the reducing condition of groundwater driven by organic carbon was extensively documented (Deng et al. 2014; Huang et al. 2012). The sample collection was conducted within an interstream area that was dominated by lacustrine facies and currently developed as farmlands and fishery ponds. The shallow aquifers comprise gray sandy silts of 7.2 to 12 m and the gray fine and yellowish medium sands below 17.2 m (Fig. 1). The textures of the upper overlaying lacustrine clayey materials led to the reducing condition of the groundwater in the area. The Dongjing River, Tongshun River, and several streams meander through the area. The groundwater tables exhibit seasonal fluctuations with around 2 months delay relative to the precipitation cycle (Deng et al. 2014).

Fifty groundwater samples were collected from the resident hand tube wells within the study area. Two river water samples were included for comparative study of spectroscopy and chemistry between surface water and groundwater (Fig. 1). Groundwater was collected after a 15-min well purging. River water was filtered using a glass syringe with a 0.45-μm membrane on the site, while groundwater was filtered in an argon-gas glove box after the samples were shipped to the laboratory. Both water samples for the DOC and DOM analyses were acidified with ultra-pure HCl to pH 2 and collected in amber glass bottles to prevent sunlight. A borehole was drilled near the center of the interstream field by using PowerProbe 9500-VTR (AMS Inc., USA). Sediment samples along the profile were collected at different intervals at depths from 6 to 22.5 m belowground. Twenty-one sediment samples with seven-segment depths (three samples for each depth) (Fig. 1) were selected for subsequent DOM extraction experiment. These procedures were performed to ensure that the collected sediments demonstrated the entire properties of aquifer materials that were in contact with shallow groundwater.

Extraction of SOM

The 0.01 M $CaCl_2$ extraction is a mild operation that is extensively performed to extract soluble organic matters in soil
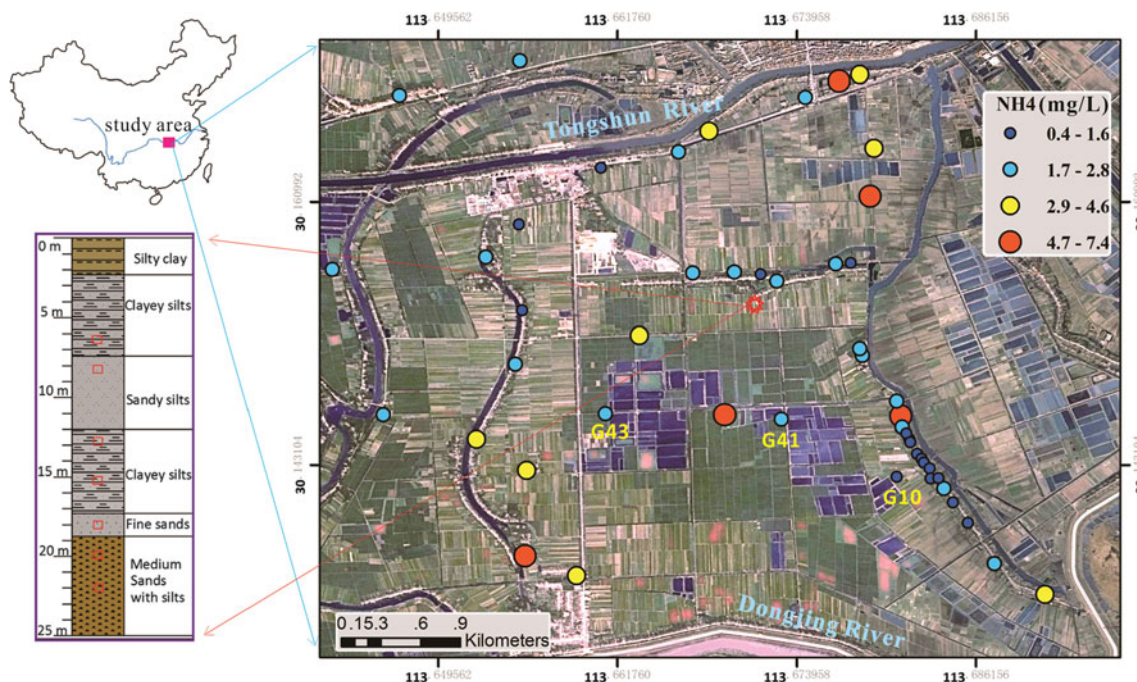
Fig. 1 Location of the study area, sampling sites of groundwater and sediments (*star symbol*), and spatial distribution of NH₄–N concentrations. Vertical sampling sites of sediments along the drilling profile is marked by *red rectangles*

solutions (Toosi et al. 2012; Zsolnay 2003). We employed this technique and assumed that the extracted OM could reflect the DOM equilibrated in pore water and represent the portion that was released from the sediment into the groundwater.

The extraction procedures were conducted based on a previous study (Kalbitz et al. 2003; Toosi et al. 2012) but under an anaerobic condition. Fresh sediment samples and N₂-purged 0.01 M CaCl₂ solutions were mixed into centrifugation tubes at a soil–solution ratio of 1:2 (*w/v*) in an anaerobic glove box under purified argon flow (<0.1 ppm O₂ and H₂O). Sealed centrifugation tubes were then shaken for 15 min at 110 rpm under room temperature. The extracted mixtures were centrifuged at 8000×*g* for 30 min, transferred back into the glove box, and then filtered with 0.45-μm Teflon syringe filters. Extraction experiments were conducted in triplicate (7 × 3), and thus, 21 sediment-extracted OM (SEOM) solutions were obtained.

Spectroscopic measurements

Fluorescence excitation–emission matrices (EEM) were measured using a fluorescence spectrometer (Hitachi F-7000, Japan) for all water samples and SEOM solutions. Emission scan was conducted from a wavelength range of 300–550 nm in 2-nm increments at a stepwise increase of 4 nm with an excitation wavelength range of 250–400 nm. A 290-nm cutoff filter was used to eliminate second-order Rayleigh scattering. High absorbance samples were measured after dilutions in anaerobic chamber until the UV₂₅₀ values were below 0.05

to minimize inner filter effects. All samples in a capped cuvette were measured in the previously mentioned glove box to avoid oxidation. The fluorescence signatures were blank subtracted using Milli-Q water from the original EEM. Fluorescence intensities were then normalized to the area under the water Raman peak. Instrument-specific excitation and emission corrections were applied to all spectra.

HIX was calculated following a suggested procedure (Zsolnay et al. 1999), which is based on the ratio of the emission scanning areas at a wavelength range of 300–345 to 435–480 nm with an excitation wavelength of 254 nm. High HIX values are associated with high C/H ratios, and thus have been used to indicate the humic character or autochthonous DOM component (Senesi et al. 1991; Zsolnay et al. 1999). The fluorescent BIX was determined by the ratio of the intensity at emissions of 380 and 430 nm at 310-nm excitation (Huguet et al. 2009). BIX allows an estimation of autochthonous biological activity in aquatic environments. The aromaticity indicator SUVA₂₅₄ reflecting aromaticity and unsaturation of DOM (Weishaar et al. 2003; Rosario-Ortiz et al. 2007) was estimated using 254 inverse meters normalized to DOC concentration in milligrams per liter. The spectra slope (S₂₇₅₋₂₉₅) over 275–295 nm was determined by fitting the spectral data to an exponential model (Helms et al. 2013). This index can be employed to reflect molecular weight distributions of DOM. A decrease in S₂₇₅₋₂₉₅ suggests an increase in molecular weight (Helms et al. 2008; Wang et al. 2014). The more detailed explanations of HIX, BIX, SUVA₂₅₄, and S₂₇₅₋₂₉₅ can be referred in the cited references.

Hydrochemical analyses

Physicochemical parameters of water samples, including temperature (T), electric conductivity (EC), pH, oxidation and reduction potential (ORP), and dissolved oxygen (DO), were measured on site using a mutiparameter handheld meter (Multi 3400, Germany). NH_4^+ was also measured on the spot via Nessler's reagent method with a HACH DR 2800 spectrophotometer. Major cations and anions were determined by an inductively coupled plasma atomic emission spectrometer (Thermo Electron, USA) and an ion chromatograph (Metrohm, Switzerland), respectively. Alkalinity was measured via titration. The charge balance errors of the inorganic ions were within 5 % for all samples.

The DOC and total nitrogen concentrations of water samples and SEOM solutions were determined by the high-temperature catalytic combustion method using a Shimadzu TOC-V$_{CPH}$ total organic carbon analyzer (Shimadzu, Co., Japan). Samples were acidified to pH <2 with HCl and were purged with CO_2-free air to remove inorganic C before measurements. Each sample was measured in triplicate and reported as mean. NH_4^+ concentrations of SEOM solutions were determined with the same methods as those used for water samples.

Data processing and analysis

Parallel factor analysis (PARAFAC) was conducted to decompose overlapped fluorophore signatures to separate peaks. PARAFAC method was described elsewhere in detail (Bro 1997; Stedmon et al. 2003) and performed using MATLAB 8.0 (Mathworks, USA). A total of 73 EEMs, including those for 52 water samples and 21 SEOM solutions, were incorporated into the modeling process. The established model was validated by split-half and residual analyses (Stedmon et al. 2003). PARAFAC components were reported as relative concentrations represented by maximum fluorescence intensity F_{max} (R.U.) or relative abundance (%). Relative abundance was calculated as the percentage of the fluorescence intensity of each component divided by the sum of the intensities of all derived components.

R-mode factor analysis (FA) was employed to identify the dominant hydrochemical variables responsible for groundwater chemistry (Güler et al. 2012; Li et al. 2014), which facilitated the understanding of the effects of NH_4^+ occurrence. A total of 24 variables, including groundwater physicochemical parameters, fluorescence intensity of DOM components (C1, C2, and C3), and spectroscopic parameters (SUVA$_{254}$, S$_{275-295}$, HIX, and BIX), were used for FA. The saturation indices (SI$_{Calcite}$, SI$_{Dolomite}$) and free-CO_2 concentration (CO_{2f}) were calculated using hydrogeochemical code PHREQC and incorporated into the dataset for FA to consider the effects of the dissolution–precipitation of carbonates. Pearson correlation of NH_4^+ with FOCs and the significance were calculated for both groundwater and SEOM samples. In addition to that for seven samples in the triplicate condition of the extraction experiment, the significance of correlation analysis was also given for the original 21 SEOM samples in supplementary material. FA, correlation analysis, and calculation of descriptive statistics were performed with SPSS 17.0.252.
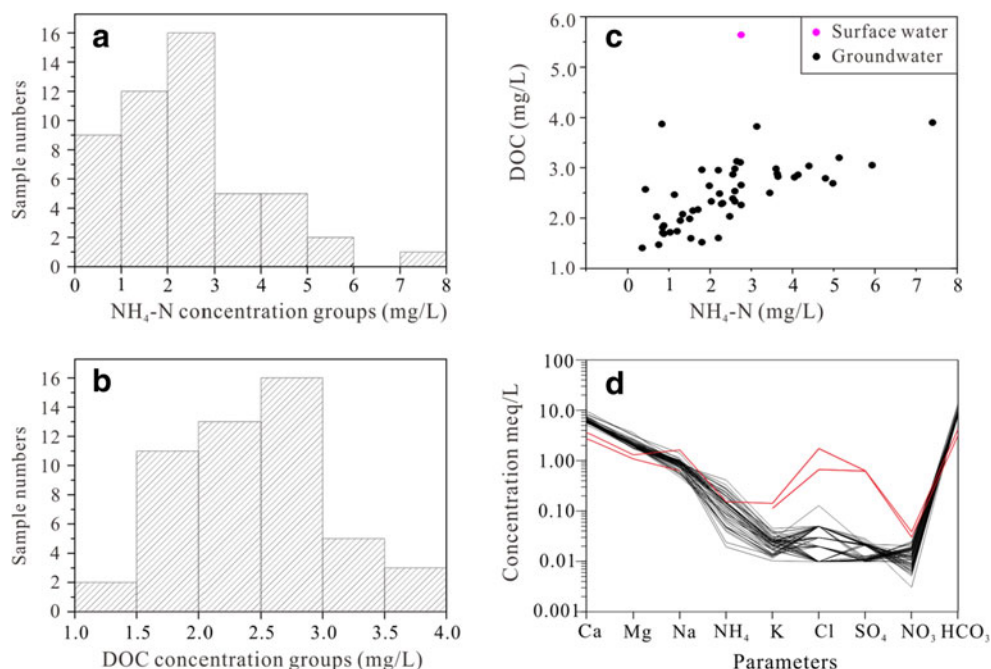
Results

N species and groundwater properties

Physicochemical measurements for groundwater and surface water are presented in Table S1. All groundwater samples were determined with NH_4–N concentrations ranging from 0.35 to 7.4 mg/L (mean 2.4 ± 1.5 mg/L), which indicates ubiquitous occurrence. About 74 % of groundwater samples (37 in 50) exhibited NH_4–N concentrations below 3 mg/L. Extremely high concentration of NH_4–N was not observed. This finding reveals a relatively consistent concentration distribution (Fig. 2a). Nitrate was not detectable except for only two samples with low concentrations of 0.3 and 0.82 mg/L, respectively (Table S1). The total nitrogen concentration determined was 0.41 to 8.0 mg/L (Table S1). This concentration value is close to that of NH_4–N although different measurement methods were conducted. Nitrite was measured by spectrophotometry [Hatch method 10207], but it was undetectable because of its low absorbance. Groundwater DOC concentrations (mean 2.5 ± 0.6 mg/L) exhibited a more centralized distribution compared with NH_4–N (Fig. 2b). A moderate correlation ($r = 0.65$, $p < 0.01$) was found between NH_4–N and DOC (Fig. 2c). One surface water sample was determined with similar concentrations of NH_4–N (2.75 mg/L) and TN (3.29 mg/L) to groundwater but higher DOC/NH_4–N than groundwater (Fig. 2c). Both surface waters had high concentrations of nitrate over 30 mg/L (Table S1).

HCO_3^- and Ca^{2+} were the dominant major anion and cation, with concentrations ranging between 474 and 832 mg/L and 103 and 193 mg/L, respectively (Table S1, Fig. 2d). The concentrations of Cl^-, SO_4^{2-}, and NO_3^- were consistently low and/or undetectable without exception of high concentrations (Fig. 2d). This result reveals a reducing and/or relatively closed environment of the local aquifer characterized by a lack of ion recharge. The reducing condition was also indicated by consistent negative ORP values and the significant amount of Fe^{2+} in the groundwater (Table S1). Two surface water samples showed evidently different ion chemistry with lower Ca^{2+}, Mg^{2+}, and HCO_3^- and higher Cl^-, SO_4^{2-}, and NO_3^- concentrations compared with the groundwater (Table S1 and Fig. 2d), which suggests anthropogenic influences.

Fig. 2 Concentrations of NH$_4$–N (**a**) and DOC (**b**) in groundwater samples. Relationship between NH$_4$–N and DOC (**c**) and major ion chemistry with groundwater samples displayed in *black line* and two surface water samples in *red line* (**d**)

PARAFAC components and relationships with ammonium in groundwater and SEOM solution

PARAFAC analysis showed three successfully decomposed FOCs (Fig. 3a–c). The validated split-analysis results are shown in Fig. S1. Several prior studies suggested that a three-component PARAFAC model sufficiently described all the fluorescence features of HS and/or DOM (Hur et al. 2014; Lee et al. 2015). The C1 component had a max Ex/Em of 250 (330–340)/440 nm, which was considered as fulvic-acid like component (FALC) (Fellman et al. 2010). The C2 component peaked at Ex/Em of ≤250(320)/390 nm with similar EEM peak range to humic-like materials (Coble 1996). Its fluorescent signature exhibited a slightly shorter Ex/Em, which could also be regarded as the blue shift peak position of FALC C1. The C3 component with a max Ex/Em of 275/340 nm was identified as a tryptophan-like fluorescence, suggesting amino acids or those free or bound in proteins, which indicate intact proteins or less degraded peptide material (Fellman et al. 2010).

An evidently stronger correlation of NH$_4$–N with FALC C1 ($r = 0.81$, $p < 0.001$, Fig. 3d) than that with bulk DOC ($r = 0.65$, $p < 0.001$, Fig. 2c) was observed for groundwater samples. The relationship with blue-shift FALC C2 ($r = 0.79$, $p < 0.01$, Fig. 3e) was slightly weaker but still significantly stronger than that with DOC. However, the positive relationship of NH$_4$–N with tryptophan-like C3 decreased relative to that with DOC. The respective stronger and weaker relationships of NH$_4$–N with FALC and tryptophan-like component C3 can be generally assumed as the two end-members of OM signature decomposed from the original moderate-correlation signature of NH4–N with DOC. By contrast, for SEOM solutions, NH$_4$–N exhibited stronger positive correlations with

FOC C1-C3 (Fig. 3g–i). The correlation trend of NH$_4$–N with FALC C1 and that with FALC C2 in SEOM solutions was observed to be a little dissimilar to that in groundwater. Since the statistical correlations of NH$_4$–N with FOC C1–C3 were at strong significance levels ($p \leq 0.001$) both for SEOM and groundwater samples (Table S2), it allows us to make comparisons of the correlations between the different systems. Our following discussion will focus on variations of correlation levels of NH$_4$–N with FOCs between sediments and groundwater other than the small difference among FOCs in either groundwater or SEOM solutions.

FA factors

Five varimax rotated factors were extracted according to the Kaiser criterion, accounting for 79.2 % of the total variance (Table 1). High positive loadings of factor 1 (F1) (representative parameters: C1, TN, C2, K$^+$, NH$_4$–N, DOC, and C3) explained the greatest amount of variance with 34.8 %, which highlights OM contribution to the groundwater chemistry (Huang et al. 2012). FOC C1–C3 incorporated into this group further demonstrated detailed indicators with specific component information for OM effects. K$^+$ was also grouped because of the strong correlation with NH$_4^+$ in which the geochemical implication is beyond the scope of this study. Factor 2 (F2) (significant variables: EC, HCO$_3$, Ca^{2+}, Mg^{2+}, and Na$^+$), which accounted for 20.9 % of the variance, was about major ion chemistry related to water–rock interactions. Parameters of pH, SI$_{Cacilate}$, SI$_{Dlomite}$, and CO$_{2f}$ with 10.2 % variance for factor 3 (F3) presented the sensitive factors for carbonate dissolution equilibrium. F4 (e.g., O$_2$ and SO$_4^{2-}$) and F5 (e.g., Fe^{2+} and ORP) clearly indicated redox effects that influenced groundwater chemistry. In general, the

Fig. 3 Spectral characteristics of three PARAFAC components and the relationships of NH4–N with each component in groundwater (*row 2*) and SEOM solutions (*row 3*)
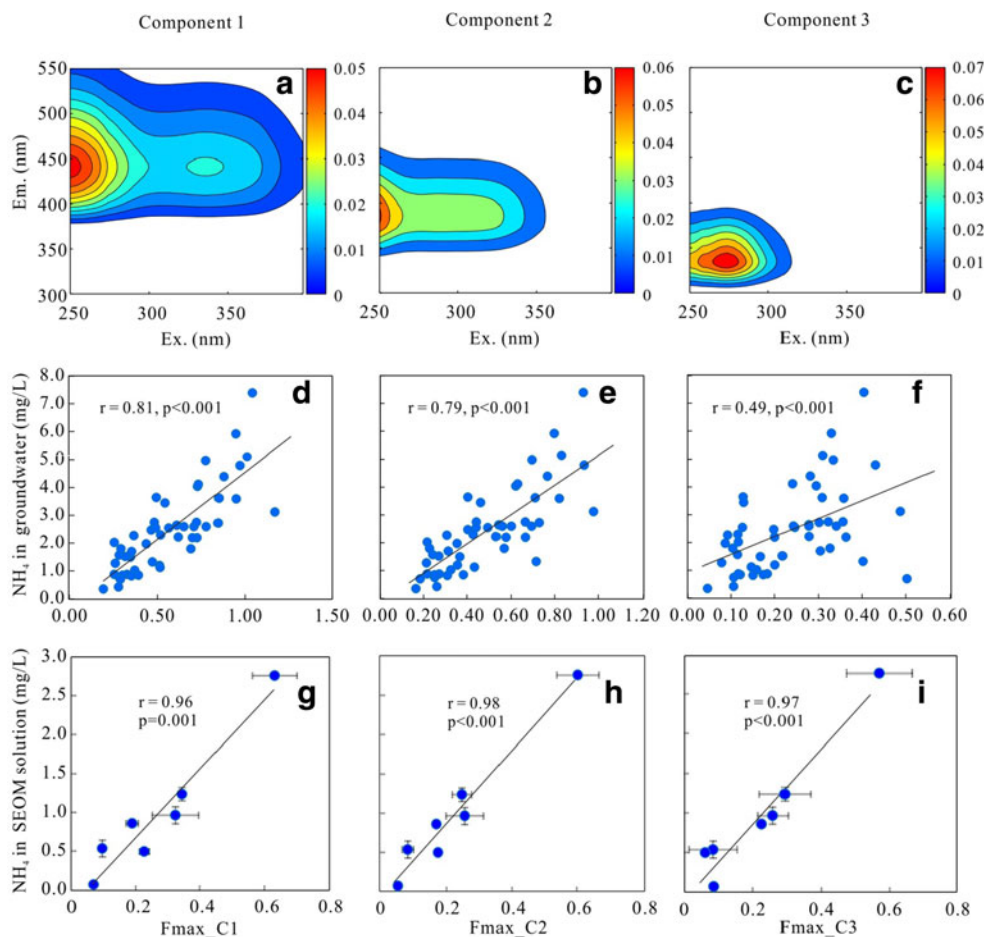
Discussions

Potential NH_4^+ sources associated with OM

In reducing groundwater, NH_4^+ could come from an inorganic source, by the dissimilatory nitrate reduction to ammonium (DNRA). However, the DNRA may result in the concurrence of NO_3^- and NH_4^+ to some extent (Hinkle and Tesoriero 2014). Thus, the ubiquitous NH_4^+ in the groundwater that accompanies the absence of NO_3^- suggests that the DNRA is unlikely to be the main source of NH_4^+ (Hinkle and Tesoriero 2014) in our groundwater. In addition, the lack of intermediate nitrogen species (i.e., NO_2^-) further suggests the inability of the reduction process to produce NH_4^+. Therefore, significant NH_4^+ sources from the reduction process of NO_3^- of infiltrated surface-water should be excluded. On the

contrary, NH_4^+-dominant nitrogen species and DOC were ubiquitously observed in the groundwater with relatively centralized concentration distribution (Fig. 2a, b) and exhibited positive relationship ($r = 0.65$, $p < 0.01$), indicating the close association of aqueous NH_4^+ with OM. The stronger correlation of NH_4–N with the fluorescent FALC than that with DOC suggests that the occurrence of NH_4^+ is associated with FALC. Despite the varying correlation levels, the positive correlations of NH_4^+ with fluorescent humic-like and amino acid-like components observed both for groundwater and SEOM solutions indicate that NH_4^+ associates with these OM components (especially FALC) at varying levels in groundwater and sediments.

In sediments/soils environments, the association of SOM and ammonium-relevant species has been established. Humic and fulvic acid are complex aromatic macromolecules with amino acids, amino sugars, peptides, and aliphatic compounds that are involved in the linkages between the aromatic groups in peats and brown coals (Demirbas et al. 2006). Amino acids and proteins comprise a large fraction of organic nitrogen in lacustrine sedimentary matter (Carstens et al. 2013) and recent soils and sediments (Demirbas et al. 2006; Friedel and Scheller 2002). NH_4^+ are either bound to negatively charged

Table 1 Varimax rotated factor loading matrix for groundwater samples

Variables	F1	F2	F3	F4	F5
C1	*0.900*	0.131	0.277	0.000	−0.200
TN	*0.893*	−0.080	0.305	−0.058	−0.032
C2	*0.871*	0.085	0.290	−0.054	−0.164
K^+	*0.858*	−0.170	0.311	−0.023	−0.031
$NH_4–N$	*0.858*	−0.086	0.304	−0.061	−0.052
DOC	*0.835*	−0.054	0.019	−0.231	0.003
C3	*0.653*	−0.042	0.068	0.044	−0.264
$S_{275–295}$	−0.532	−0.104	−0.052	−0.370	0.507
EC	−0.015	*0.983*	0.029	0.085	−0.042
HCO_3^-	−0.069	*0.978*	−0.031	0.096	0.031
Ca^{2+}	−0.283	*0.899*	−0.181	0.065	0.095
Mg^{2+}	−0.099	*0.809*	−0.038	0.086	−0.108
Na^+	0.352	*0.729*	0.147	−0.032	0.063
pH	−0.380	−0.168	*−0.883*	0.023	0.111
$SI_{Cacilate}$	−0.400	0.346	*−0.831*	0.073	0.100
$SI_{Dlomite}$	−0.425	0.318	*−0.826*	0.054	0.136
CO_{2f}	0.345	0.500	*0.748*	0.015	−0.078
O_2	−0.085	0.144	−0.090	*0.848*	0.050
SO_4^{2-}	−0.219	0.058	0.024	*0.727*	0.121
$SUVA_{254}$	0.157	−0.070	−0.070	*0.627*	−0.553
Fe^{2+}	0.151	0.119	0.254	−0.045	*−0.698*
ORP	0.002	0.245	−0.009	0.467	*0.668*
BIX	−0.191	−0.217	−0.055	−0.159	0.284
HIX	−0.027	0.288	0.375	−0.273	0.158
Eigenvalues	8.34	5.01	2.45	1.78	1.42
Variance	34.75	20.89	10.21	7.41	5.91
C. variance	34.75	55.6	65.85	73.26	79.17

The italicized values marked in each column represent the significant correlation coefficients of parameter variables with each factor (F1-F5)

sites of phenolic-OH and carboxylic-COOH groups of aromatic humic acid and fulivc acid or produced by mineralization processes of amino acids (e.g., urea hydrolyses) (Reeza et al. 2009). Thus, both aromatic OMs (e.g., the C1 and C2) and amino-group complexes have close affinities with NH_4^+. Our geochemical analyses of sediment nitrogen showed high portions of Kjeldahl-N (93.6–99.4 %) in sediment nitrogen pool and significant amounts of $NH_4–N$ (mean 6.7 %) (unpublished data) which probably suggested the similar associations of nitrogen with OMs as established. Therefore, the correlation of NH_4^+ from groundwater with FOC agrees with established relationships of nitrogen–OM in sediments and thus suggests the potential of SOM as the source of NH_4^+ of groundwater. The declining NH_4^+-OMs relationships from the stronger in sediments (Fig. 3g–i) to the relatively weaker in groundwater (Fig. 3d–f) will be discussed further later.

Hydrogeology of our study area features a seasonal water table dynamics affected by surface water and/or (possible) the presence of surface-constructed ponds. Studies in Bangladesh with the similar hydrogeology (Harvey et al. 2002; Neumann et al. 2010) showed that recharged water from ponds induced by irrigation pumping transfers degradable organic carbon to shallow aquifers. Thus, DOC in the surface-water bodies in our study area may be a possible source to N-bearing DOM of groundwater. Hydrochemical analyses showed that, in addition to SO_4^{2+} and NO_3^-, conservative Cl^- in the groundwater remained in significantly lower concentrations (mostly below 2 mg/L) compared with that in surface water (23.30 and 64.21 mg/L, Table S1). Moreover, several samples collected from the wells at the ponds (G10, G41, and G43 in Fig. 1) did not exhibit a substantially high concentration of NH_4^+ (or DOC) (Fig. 1 and Table S1). Apparently, the surface infiltration of N-bearing DOM (or Cl^-) into the groundwater did not readily occur at the presented aquifer condition. Significant arguments (Aggarwal et al. 2003; Datta et al. 2011; van Geen et al. 2003) on the pond-derived organic carbon sources have been presented since Harvey's proposal (Harvey et al. 2002). Reactive transport modeling (Datta et al. 2011) considering DOM adsorption/desorption indicated that the transport time of pond-derived DOM to deep aquifers exceeds typical young groundwater ages of a few decades by thousands of years. For our study, the depletion of Cl^- and NH_4^+-bound OM of groundwater underlying ponds could be attributed to the retardative effect of the fine texture of clayey materials of aquitards (Fig. 1) on the transport of DOM in spite of existing flow passage between surface water and groundwater.

SOM sources of NH_4^+ are found for typical Quaternary aquifer systems, even the sandy aquifers. Studies conducted on a sandy aquifer (Hinkle et al. 2007) in Oregon and selected principal aquifers in 48 contiguous states in the USA (Hinkle and Tesoriero 2014) suggested that NH_4^+ mobilization occurs from the degradation of aquifer organic matter in most sites. Our previous study (Huang et al. 2015) demonstrated the close similarity of the spectroscopic properties of DOM between groundwater and sediments. The transformation patterns of groundwater DOM (GDOM) for various samples and the analyzed hydrochemical processes integrally qualified SOM as the source of GDOM. Therefore, our data synthetically support the source of aquifer sediments for the OM-associated NH_4^+ of the groundwater. However, the potential contribution of leaching DOM from the bottom sediments of surface ponds to the NH_4^+ at sites where the top "open-doors" of aquifers exist cannot be completely ignored, which were not detected in the current study (Huang et al. 2015).

OM biodegradation effects on NH_4^+–OM concurrence

One of the most important highlights by FA is the contribution of N-associated OM to groundwater chemistry suggested by F1 parameters (TN, $NH_4–N$, DOC, C1, and C2), which could
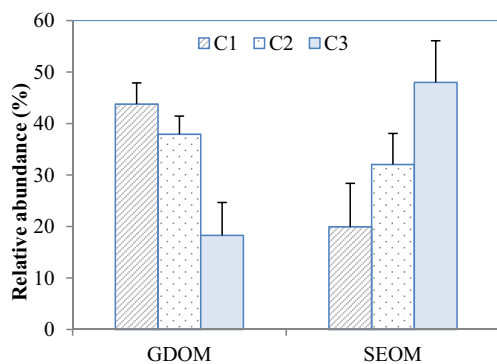
**Fig. 4** Relative abundance of PARAFAC components in GDOM and SEOM

be related to the reducing characteristic of the groundwater as suggested by the parameters in F4 and F5 (i.e., depleted dissolved oxygen and SO_4^{2-}, negative ORP and ubiquitous Fe^{2+}). Available electron acceptors with utilizable organic carbon (electron donors) can catalyze the biodegradation of OM and promote the prevalence of reducing condition in aquifers (Stumm and Morgan 1996). Lithologic sources of DOC, instead of those surface-derived, are important sources of electron donors in shallow groundwater (Green et al. 2008; Tesoriero and Puckett 2011). Otherwise, as stated in the previous discussion, the N-associated humic materials are typically composed of soil/sediment OM components. Therefore, TN, NH_4–N, and DOC grouped with FOCs as the F1 for FA (Table 1) may indicate the involvement of the N-associated SOM in bio-redox degradation processes in the aquifer.

Several data can be drawn to evaluate the biodegradation potential of SOM. The dominant relative abundance of shorter wavelength FOCs (C3 and C2, Fig. 4) of SEOM indicates a relatively simpler structure and/or lower molecular size of SOM (Lee et al. 2015; Mostofa et al. 2013) compared with that of groundwater. The simpler, smaller molecular structure and/or microbial degradation effect were commonly used to explain the blue shifts (indicating shorter wavelengths) of fluorescence peaks (Fellman et al. 2010; Helms et al. 2013). Shorter wavelength component (i.e., C3) with microbial signatures of DOM can be linked because C3 is assigned as protein/ammonia

acid-like materials. Otherwise, the more liable DOM signatures of SEOM solutions were also suggested by spectroscopic indices that include higher $S_{275–295}$ (smaller molecular weight), lower $SUVA_{254}$ (lower aromaticity), higher BIX, and lower HIX (strong microbial sources) (Fig. S2). The information above implies that the liable small molecular fractions available from sediments (e.g., NH_4-associated protein-like fraction) can be preferentially utilized by the potential biodegradation after diffusion to groundwater, whereas the relatively refractory humic-like substances (e.g., C1 and C2) were less modified and thus tend to be preserved. The varying distributions of relative abundance of FOCs among sediments and groundwater corresponding to biodegradation labilities were consistent with the maintenance of a relatively good relationship of NH_4–N and FALC (C1 and C2) and the evident decline of the relationship of NH_4 with protein-like OM (C3) (Fig. 3d–j and Table S2) compared with groundwater to SEOM solution.

The significant physicochemical parameters grouped in F2 (e.g., EC, HCO_3^-, Ca^{2+}, Mg^{2+}) suggest that abiotic hydrogeochemical process is responsible for the occurrence of HCO_3^- in groundwater, which was mainly associated with mineral weathering, that increases HCO_3^- with Ca^{2+} and Mg^{2+} (Gaillardet et al. 1999). However, biotic OM degradation can also contribute to HCO_3^- geneses in groundwater (Stumm and Morgan 1996). To explore the influence of OM degradation on the occurrence of NH_4^+ and fulvic-like OMs, the normalized concentration of HCO_3^- to the sum of ($Ca^{2+}+Mg^{2+}$) (in mmol/L) was adopted to reflect HCO_3^- trends resulted from OM biodegradation. The accompanying increase of FALC C1 and NH_4–N concentration (scaled balls) with normalized HCO_3^- concentration ($r=0.68$, $p<0.01$) (Fig. 5a) and [H^+] ($r=0.64$, $p<0.01$) (Fig. 5b) were both observed. The results suggested that the biodegradation of complex OM produced FALC organic compositions and NH_4^+ from the aquifer OM precursor and increased HCO_3^- and protons in groundwater. Fulvic-like OM, HCO_3^-, H^+, and NH_4^+ are common products of various OM reactions. The macromolecular humic acids/substances can be transformed into lower molecular size acidic fulvic acids and/or other forms of organic acids through anaerobic biodegradation

Fig. 5 Relationship of FAL C1 concentration with normalized HCO_3^- concentration (**a**) and [H^+] (**b**); ball sizes were scaled to NH_4–N concentrations suggesting co-increase of NH_4–N with FAL C1
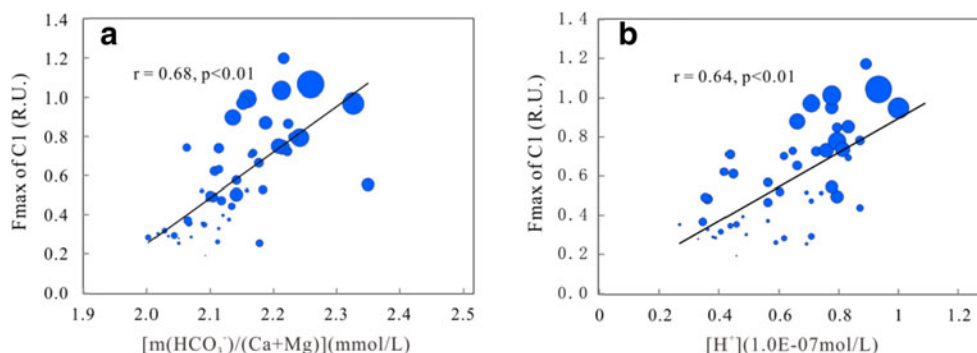
(Lechtenfeld 2012). The mineralization of organic nitrogen can release NH_4^+ through the hydrolysis effect of amino acids by hydrolytic bacteria (Koho et al. 2013). Finally, the oxidative degradation of labile organic carbon (normally the smaller molecules) produces HCO_3^- or CO_2. The presented relationships of FALC and NH_4^+ with HCO_3^- and H^+ indicate the couple effects of these reactions that may simultaneously occur in the aquifer.

Conclusions

This study is the first to investigate the concurrence of NH_4^+ with FOCs in the groundwater of a fluvio-lacustrine aquifer at the Central Jianhan Plain by using fluorescent spectroscopic and hydrochemical methods. Results indicated the accompanying occurrence of NH_4^+ with FALC in the groundwater, which were mainly associated with the biodegradation of SOM.

Nitrogen contamination of water bodies is commonly attributed to anthropogenic sources, such as sewage and agricultural and industrial wastes. However, the natural occurrence of NH_4^+-N in aquifers is receiving increasing attention because of its potential high loadings for nitrogen species transformations and subsequent negative effects on health and environment. Employing 3D fluorescence spectroscopy with hydrochemical analysis allows us to link NH_4^+ with FOCs and groundwater physicochemical parameters. The results facilitate the interpretation on the relationship of NH_4^+ with specific FOC types and provide new insights into NH_4^+ genesis in OM-rich aquifers.

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