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M.A. Robinson-Lora and R.A. Brennan: Chitin complex for the remediation of mine impacted water: Geochemistry of metal removal and comparison with other common substrates 336

T. Le Druillennec, G. Ielsch, O. Bour, C. Tarits, G. Tymen, G. Alcalde and L. Aquilina: Hydrogeological and geochemical control of the variations of ^{222}Rn concentrations in a hard rock aquifer: Insights into the possible role of fracture-matrix exchanges 345

A. Ohta, N. Imai, S. Terashima, Y. Tachibana, K. Ikehara, H. Katayama and A. Noda: Factors controlling regional spatial distribution of 53 elements in coastal sea sediments in northern Japan: Comparison of geochemical data derived from stream and marine sediments 357

K. Ndung'u, S. Friedrich, A.R. Gonzalez and A.R. Flegal: Chromium oxidation by manganese (hydr)oxides in a California aquifer 377

E. Lehne, V. Dieckmann and B. Horsfield: Comparison of bulk kinetic parameters for asphaltenes from long-time stored and related fresher-produced crude oils 382

H. Tan, G. Zhang, P.J. Heaney, S.M. Webb and W.D. Burgos: Characterization of manganese oxide precipitates from Appalachian coal mine drainage treatment systems 389

A. Davis, K. Heatwole, B. Greer, R. Ditmars and R. Clarke: Discriminating between background and mine-impacted groundwater at the Phoenix mine, Nevada USA 400

O.S. Pokrovsky, A. Feurtet-Mazel, R.E. Martinez, S. Morin, M. Baudrimont, T. Duong and M. Coste: Experimental study of cadmium interaction with periphytic biofilms 418

H.-C. Chao, C.-F. You and C.-H. Sun: Gases in Taiwan mud volcanoes: Chemical composition, methane carbon isotopes, and gas fluxes 428

P.C. Blaser, M. Coetsiers, W. Aeschbach-Hertig, R. Kipfer, M. Van Camp, H.H. Loosli and K. Walraevens: A new groundwater radiocarbon correction approach accounting for palaeoclimate conditions during recharge and hydrochemical evolution: The Ledo-Paniselian Aquifer, Belgium 437

S.G. Osborn and J.C. McIntosh: Chemical and isotopic tracers of the contribution of microbial gas in Devonian organic-rich shales and reservoir sandstones, northern Appalachian Basin 456

Continued on outside back cover

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Abiotic interactions of natural dissolved organic matter and carbonate aquifer rock

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ABSTRACT

Abiotic interactions between natural dissolved organic matter (NDOM) and carbonate aquifer rock may be controlling factors of biogeochemical processes and contaminant fate in carbonate aquifer systems. The importance and effects of these interactions were examined using batch adsorption experiments of soil NDOM and representative carbonate sorbents from the Floridan Aquifer. Adsorption of NDOM carbon to aquifer rocks was well-described using a modified linear model and was mostly reversible. Significant adsorption was observed at higher NDOM concentrations, while the release of indigenous organic matter from the rocks occurred at lower concentrations. Longer interaction periods led to more adsorption, indicating that adsorption equilibrium was not achieved. For relatively pure carbonate rock samples, sorbent surface area was found to be the most important controlling factor of adsorption, whereas the presence of indigenous organic matter and subdominant mineral phases were more important, when they occurred. Preferential adsorption of a high over low molecular weight and humic over fulvic components of NDOM onto carbonate sorbents was detected using liquid size exclusion chromatography and excitation–emission fluorometry, respectively. The presence of NDOM inhibited mineral dissolution, though this inhibition was not proportional to NDOM concentration as surface area and mineralogy of carbonate sorbents played additional roles. Though the NDOM–carbonate rock adsorption mechanism could not be completely determined due to the heterogeneity and complexity of NDOM and sorbent surfaces, it is speculated that both rapid and weak outer-sphere bonding and stronger but slower hydrophobic interaction occur. These results have important implications for groundwater quality and hydrogeologic projects such as aquifer storage and recovery.

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1. Introduction

Carbonate aquifers are important as they cover 17% of the land surface in the USA and provide 25% of the drinking water supplies to the global population. Because of their often high permeability and thus, close connectivity to the surface, they receive relatively large fluxes of organic matter (OM) as well as contaminants (Lau and Mink, 1987). Natural dissolved organic matter (NDOM), a ubiquitous component of natural waters derived mainly from microbes and plants and their degradation products, is complex and heterogeneous in nature with a wide range of molar masses and chemical structures (Frimmel, 1998).

Groundwater NDOM, and its interactions with carbonate aquifer constituents, may play an important role in controlling subsurface processes by acting as a proton donor and acceptor and as a pH buffer, by influencing mineral precipitation and dissolution, and by affecting the transport and degradation of pollutants (Findlay et al., 2003; Frimmel, 1998; Schlautman and Morgan, 1994). In addition, NDOM–carbonate mineral interaction is likely to be a controlling factor in groundwater quality in the course of hydrogeologic projects such as aquifer storage and recovery (ASR) and soil-aquifer treatment (SAT) (Arthur et al., 2002; Cha et al., 2004; Drewes et al., 2006; Lindroos et al., 2002; Pavelic et al., 2005; Rauch and Drewes, 2004). Despite its importance in these critical areas, scientific study of NDOM–carbonate interaction mechanisms and consequences has been limited.

Among the abiotic NDOM–mineral interactions that may take place in carbonate aquifers are adsorption/desorption and dissolution/precipitation. Adsorption of organic compounds onto inorganic solid surfaces significantly alters the physiochemical properties of the underlying solid whose behavior may become dominated by the adsorbed NDOM (Davis, 1982). Due to their high surface area and homogeneity, metal oxides (e.g. Gu et al., 1994; Johnson et al., 2004) and clay minerals (e.g. Baham and Sposito, 1994; Wang and Xing, 2005) are often the subject of OM adsorption investigations. In contrast, adsorption of organic compounds onto calcite (the major constituent of carbonate aquifers) has not been extensively investigated, though a few studies have reported significant adsorption. For example, the adsorption of benzoate, citrate, tartrate and glutamate onto calcite imparted a negative surface charge to calcite (Plank and Bassioni, 2007). Adsorption of Suwannee River humic acid (SRHA) onto calcite was reported as rapid and mostly irreversible, with corresponding changes in

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electrostatic properties (Lee et al., 2005), and depletion in organic acidic compounds in NDOM following calcite adsorption was ascribed to be preferential adsorption of these compounds (Carter, 1978). However, no studies have examined the interaction of NDOM with more 'realistic' carbonate aquifer materials.

Another unique feature of carbonate, versus other types of aquifers, is that dissolution/precipitation may occur on short (experimentally observable) timescales. Enhanced carbonate dissolution is an environmental concern of NDOM–carbonate interaction in a carbonate aquifer, since it leads to geological hazards such as land surface subsidence (Wu, 2003). Many have pointed out that some organic compounds can enhance dissolution or at least inhibit precipitation (Inskeep and Bloom, 1986; Luttge and Conrad, 2004; McMahon et al., 1995; Perry et al., 2003; Wu and Grant, 2002). Both the protons released by acidic moieties of NDOM and the CO_2 produced via heterotrophic microbial activity can enhance carbonate mineral dissolution. On the other hand, it has been shown that other organic compounds inhibit carbonate dissolution (Frye and Thomas, 1993; Thomas et al., 1993), possibly due to surface protection.

The main purpose of this study was to examine subsurface abiotic NDOM–carbonate interaction using experimental conditions and materials similar to those found in the Floridan aquifer system (FAS). Thus, north Florida forest soil NDOM extracts were used as sorbate and various carbonate samples (quarry and core materials) from a range of FAS geologic formations were used as sorbents. Two sorbent size fractions and NDOM concentrations spanning the natural NDOM concentration range were combined in batch adsorption experiments. Chemical analyses of the solute composition before and after carbonate interaction were used to understand the role of abiotic processes in NDOM transformation during aquifer transit. The present study is designed to be a starting point toward an understanding of the range and complexity of behaviors in an OM-carbonate subsurface system.

2. Materials and methods

2.1. Sorbents

Adsorption experiments were carried out using two groups of aquifer materials: Floridan Aquifer core material provided by the Florida Geological Survey (FGS) from regions of south-central Florida where ASR projects are underway, and relatively pure Floridan quarry materials provided by the Florida Department of Transportation (FDOT) (designated C and Q, respectively: Table 1, Appendix Table A1). Before granulating, the FDOT aquifer carbonate samples were massive and relatively light in color compared to FGS core materials, which were friable and brownish in color. The samples include representatives from each of these four major geologic formations of the Upper Floridan Aquifer: Hawthorn Group, Suwannee Limestone, Ocala Limestone, and Avon Park Formation (designated H, S, O and A, respectively).

All samples were granulated and then sieved into <0.15 mm and 0.15–0.5 mm size fractions prior to surface area, compositional determinations, and adsorption experiments. Smaller particle sizes were required to facilitate sorption experiments rather than to mimic field conditions. Particle surface area was determined by multipoint N_2 adsorption using a Quantachrome A1 Autosorb and Brunauer–Emmett–Teller (BET) theory (Brunauer et al., 1938). Surface areas were low, ranging from 0.5 to 13 m^2/g and none of the samples contained significant microporosity (Table 1). Sorbent major mineralogy was identified using a Rigaku Ultima IV X-ray diffractometer (XRD) with an X-ray generator working at a power of 40 kV and 44 mA. Diffraction patterns were recorded in the range of 5–60° 2θ with steps of 0.02° 2θ and a counting time of 3 s/step. The quarried carbonate samples, Q–O and Q–S are nearly pure calcite. Of the core materials, C–O samples are nearly pure calcite, C–A sample nearly pure dolomite, C–S mainly calcite and quartz, and the C–H sample had calcite, dolomite, quartz, apatite and palygorskite (detailed in Appendix Fig. A1). The OM content of both FGS and FDOT samples was measured by loss-on-ignition (LOI, 450 °C for 4.5 h) and converted to organic C (OC) content assuming an average of 0.5 g OC/g OM (Essington, 2004). The C–H sample had a surface area and OC content significantly greater than the others, while the OC content of both quarry samples were clearly lower than that of all core samples (Table 1).

2.2. Sorbates

Three different types of north Florida NDOM (soil, stream and lake NDOM) were collected and chemically analyzed, but only soil NDOM was selected for further investigation since all NDOM samples were found to be of similar chemical composition (i.e., spectrofluorometrically and molecular weight (M_w) distribution using fluorometry and liquid chromatography, respectively). The selection of a soil extract as the primary NDOM source for adsorption experiments was also based on the consideration that most NDOM in groundwater is likely to be soil-derived (Tipping et al., 1997). A north Florida mixed forest soil (collected at 29°36′04″N 82°21′42″W) was mixed with water (soil/water volume ratio ~1:2) in a polycarbonate container and placed on an end-over-end shaker for 4 to 5 days. The soil–water mixture was then centrifuged at 4000 rpm for 5 min and the supernatants were filtered (0.45 μm membrane, Millipore) and then concentrated by freeze-drying (not to dryness). Extracts were stored in the dark at 4 °C, prior to dilution with deionized (DI) water (also photo-oxidized

Table 1
Surface area and organic C composition of the Upper Floridan Aquifer sorbents used in this study.

Sample code	Geologic formation	Sorbent surface area (m^2/g)[c]		Organic C content (wt.%)[d]
		<0.15 mm size fraction	0.15–0.5 mm size fraction	
Core samples[a]				
C–H	Hawthorn	9.6	13	1.29
C–S	Suwannee	3.9	4.1	0.38
C–O	Ocala	0.7	1.7	0.74
C–A	Avon Park	0.6	0.5	0.66
Quarry samples[b]				
Q–S	Suwannee	3.7	2.8	0.02
Q–O	Ocala	1.5	0.8	0.11

[a] Core samples provided by the Florida Geological Survey (FGS), Tallahassee, FL.
[b] Quarry samples provided by Florida Department of Transportation (FDOT), Tallahassee, FL.
[c] Sorbent surface area (m^2/g sorbent) determined using multipoint N_2 adsorption and calculated using BET theory.
[d] Sorbent organic C content (weight %) determined by loss-on-ignition (LOI) method (assuming average organic matter composition of 50% organic C).

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OC-free) to prepare sorbate NDOM solutions of various concentrations. The pH of the NDOM background solution was measured to be slightly acidic, while the ionic strength of the solution was not determined. The solutions were not sterilized in any way throughout the extraction and preparation processes.

2.3. Batch adsorption and desorption experiments

Batch adsorption experiments were prepared by mixing 40 mL background NDOM solutions (concentrations ranging from 0 to 153.49 mg C/L) with an amount of granulated aquifer material with 20 m^2 surface area (weights ranging from 2.08 to 39.98 g) in 50 mL polypropylene centrifuge tubes. Tubes were then place in horizontal position on a shaker table (200 rpm) for 2–4 days at room temperature (22 ± 2 °C). At the completion of the adsorption period, the suspensions were centrifuged at 4000 rpm for 5 min, and the supernatants were immediately pipetted into combusted glass vials and stored in the dark at 4 °C prior to chemical analyses. Duplicate reaction tubes, along with controls with no sorbent, were prepared for each NDOM concentration. Desorption studies were also conducted on selected samples. After removal of the supernatant following the adsorption phase, tubes were weighed so that entrained solution amount could be calculated, and 40 mL OC-free DI water was added to each tube.

The amount of dissolved organic C (DOC) adsorbed onto or desorbed from sorbents was assumed to be the difference between DOC in starting and ending solutions. DOC was measured on a total organic carbon analyzer (Shimadzu TOC-5000A) after acidifying to pH 1–2 with 1 M HCl and sparging for 2 min with OC-free air to remove inorganic C from samples prior to the measurement. The mean of 3–5 injections of 60 μL is reported for every sample and the coefficient of variance was <5% for replicate injections.

2.4. Chemical analyses

The composition of NDOM in sorbate solution before and after adsorption experiments was examined by a variety of methods in order to determine the chemical nature of the adsorbed OM. Spectroscopic characteristics were examined using a Hitachi F-7000 fluorometer equipped with a Xe lamp to obtain three-dimensional excitation–emission matrix (EEM) spectra of the samples. Analyses were performed at a constant temperature of 22 ± 2 °C. Excitation wavelengths from 200 to 400 nm incremented at 10 nm intervals were collected, chosen as a compromise between data resolution and data collection time. For each excitation wavelength, emission was measured from 200 to 600 nm at 3 nm intervals. The scan speed for all samples was set at 60,000 nm/min.

The M_w distribution of NDOM before and after adsorption was determined by high performance liquid chromatography-size exclusion chromatography (HPLC-SEC). The HPLC system consisted of a solvent pump (Shimadzu LC-20AT5) and a UV–VIS detector (Shimadzu SPD-20A). The SEC column used was a TSK-GEL® $G3000_{SW}$ (30 cm × 7.8 mm diameter, Tosoh Bioscience LLC) and compound detection was by UV-absorbance at 254 nm. A phosphate buffer was used as a mobile phase (0.1 M NaCl, 0.002 M KH_2PO_4, and 0.002 M K_2HPO_4 buffered to pH 6.8) and flow rate was 1 mL/min. The M_w calibration function was obtained using 4 protein standards: bacitracin (M_w = 1.45 kD), chymotrysinogen A (24 kD), ovalbumin (45 kD), and albumin bovine (67 kD):

$$M_w = -10.93 \times \text{retention time} + 158.57$$

R^2 = 0.986. M_w is in kD and retention time in minutes.

Concentrations of the cations (Ca^{2+} and Mg^{2+}) of the background solution, both before and after adsorption, were measured using an automated Dionex DX500 ion chromatograph (IC), in order to detect possible mineral dissolution/precipitation reactions. Samples for IC analysis were acidified to pH = 1–1.5 immediately after centrifugation and were then stored at 4 °C prior to analysis (within 7 days). NDOM loss was not determined, but it is considered to be negligible given the short storage time. Internal standards reflect a precision of better than 3% of the value of the measurement.

2.5. Adsorption and desorption isotherms

Adsorption and desorption isotherms were constructed by plotting the amount of DOC adsorbed or desorbed versus equilibrium NDOM concentration. The adsorption isotherm data were fit to three empirical adsorption models (linear, Freundlich and Langmuir) and quantified using least squares techniques (Table 2 and Appendix Table A2). Although these three models can fit the data equally well (i.e. high R^2), the linear model is the simplest model and makes the fewest assumptions, thus, was chosen as best in keeping with the principle of parsimony. Further, a simple model is more easily applied to estimations of NDOM–carbonate adsorption in natural hydrogeologic systems where, in many instances, the amount of data available is insufficient to justify a more sophisticated approach. Lastly, some more complex adsorption models, including Freundlich and Langmuir, may be reduced to linear model under certain restrictive assumption or at lower sorptive concentration ranges. In this study, the data were fit using a slightly modified linear equation, which includes a y-axis intercept term which was needed to express the amount of indigenous OM released from the aquifer materials:

$$q_e = k_D C_e + b$$

where q_e is the amount of adsorbed NDOM normalized to sorbent weight (in mg C/g sorbent) or surface area (in mg C/m^2 sorbent), and C_e is the equilibrium organic C concentration in the background solution (in mg C/L). The distribution coefficient, k_D (in L/g or L/m^2 sorbent), is a function of the properties of the sorbent and sorbate interaction and is an indication of the sorbent adsorption affinity (Schwarzenbach et al., 2003).

3. Results

3.1. Quantity of NDOM adsorbed by carbonate rock

Adsorption isotherms for NDOM on granulated quarry materials (Q–S and Q–O) of two grain sizes (<0.15 and 0.15–0.5 mm) and two time periods (2 and 4 days) are linear or near-linear (average R^2 value of 0.995, Fig. 1) in a NDOM concentration range extending from 0 to at least 153 mg C/L (Fig. 1, model parameters in Table 2). In all cases, Q–S exhibited greater adsorption affinity (higher k_D) than Q–O. Within rocks of the same geologic formation, the sorbents of the finer size fraction (<0.15 mm) had a larger k_D than their 0.15–0.5 mm counterparts when expressed on a weight-normalized basis. There was no significant difference in k_D values, however, expressed on a surface-area-normalized basis (Table 2). No significant pH change was detected over the course of the 4-day adsorption, as well as desorption period.

For these quarry materials, longer NDOM–carbonate interaction periods (i.e. 4 versus 2 days) produced greater k_D values, though individual data points for 2 versus 4 day adsorption were not always significantly different. Therefore, the NDOM–carbonate adsorption system did not, by definition, reach equilibrium in 2 or likely even 4 days, and the full adsorption capacities of the sorbents remain unknown. Longer time period adsorption experiments were not carried out, however, due to very small additional amount of NDOM adsorbed between day 2 and 4, as well as due to the possibility of mineral dissolution. In addition, since the authors were more interested in reproducing the subsurface

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Table 2
Linear model parameters for sorbent-NDOM isotherms (both weight-normalized and surface area-normalized adsorption).

Experimental treatment[a]	Weight-normalized		Surface area-normalized		R^2
	k_D[b]	b[c]	k_D	b	
Q–S,<0.15 mm, 4-day, adsorption	0.005	−0.011	0.002	−0.003	0.997
Q–S,<0.15 mm, 2-day, adsorption	0.005	−0.012	0.001	−0.003	0.994
Q–S, 0.15–0.5 mm, 4-day, adsorption	0.004	−0.015	0.002	−0.006	0.994
Q–S, 0.15–0.5 mm, 2-day, adsorption	0.003	−0.009	0.001	−0.003	0.995
Q–O,<0.15 mm, 4-day, adsorption	0.002	−0.003	0.001	−0.002	0.995
Q–O,<0.15 mm, 2-day, adsorption	0.002	−0.016	0.001	−0.011	0.999
Q–O, 0.15–0.5 mm, 4-day, adsorption	0.001	−0.005	0.001	−0.010	0.993
Q–O, 0.15–0.5 mm, 2-day, adsorption	0.001	−0.008	0.001	−0.007	0.996
C–H, 0.15–0.5 mm, 2-day, adsorption	0.012	−0.033	0.001	−0.003	0.991
C–S, 0.15–0.5 mm, 2-day, adsorption	0.011	−0.061	0.003	−0.015	0.942
C–O, 0.15–0.5 mm, 2-day, adsorption	0.013	−0.153	0.008	−0.092	0.977
C–A, 0.15–0.5 mm, 2-day, adsorption	0.005	−0.050	0.011	−0.102	0.432
Q–S,<0.15 mm, 4-day, desorption	0.005	0.004	0.002	0.001	1.000
Q–S, 0.15–0.5 mm, 4-day, desorption	0.003	0.004	0.001	0.002	1.000
Q–O,<0.15 mm, 4-day, desorption	0.002	0.004	0.001	0.002	1.000
Q–O, 0.15–0.5 mm, 4-day, desorption	0.001	0.004	0.001	0.006	1.000

[a] Treatment listed as sorbent type, particle size, interaction time period, and experimental stage.
[b] k_D is the slope (distribution coefficient) for the linear model (for weight-normalized adsorption: L/g sorbent, and for surface area-normalized adsorption: L/m^2 sorbent).
[c] b is the y-axis intercept of the linear model (for weight-normalized adsorption: mg C/g sorbent, and for surface area-normalized adsorption: mg C/m^2 sorbent).

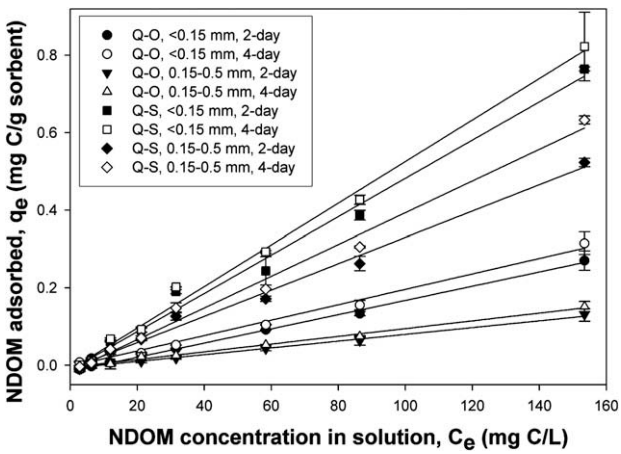

Fig. 1. Adsorption data for NDOM on Q–O and Q–S carbonate rocks of two grain size fractions (<0.15 and 0.15–0.5 mm) and for 2 and 4 day interaction periods. Error bars represent the standard deviation of duplicate analyses. The solid lines are the linear model adsorption isotherms.

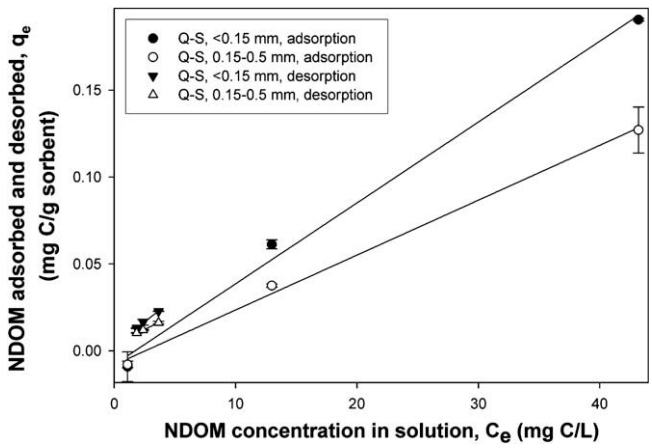

Fig. 2. Adsorption and desorption data for NDOM on Q–S of two grain sizes (<0.15 and 0.15–0.5 mm), 4-days. Error bars represent the standard deviation of duplicate analyses. Solid lines are the linear model fit of adsorption and desorption isotherms.

environment and investigating the NDOM adsorption character, 4 days appears to be is a suitable time span for these adsorption experiments.

Immediately after the 4-day adsorption, a 4-day desorption experiment for Q–S and Q–O was also carried out using OC-free DI water to replace the NDOM solution. Since both rocks have similar adsorption–desorption patterns, only Q–S (both <0.15 mm and 0.15–0.5 mm) is shown (Fig. 2). At the low solution concentrations at which desorption was carried out, a small portion of the NDOM remained sorbed to the quarry materials. That is, a small amount of hysteresis was observed, indicating that adsorption was not perfectly reversible.

Two-day adsorption isotherms for NDOM (0–20 mg C/L) adsorbed on all 6 aquifer sorbents (C–S, C–H, C–A, C–O, Q–O and Q–S, all of 0.15–0.5 mm grain sizes) are plotted in Fig. 3 (model parameters in Table 2). In general, the FGS core materials sorbed more NDOM than FDOT quarry materials at the same background NDOM concentrations, indicating a greater adsorption affinity for the core materials. The isotherm linearity for quarry materials (average $R^2 = 0.995$) was better than that of FGS core material (average $R^2 = 0.970$, excluding C–A). The unexpectedly poor linearity for C–A is not likely caused by experimental error since exper-

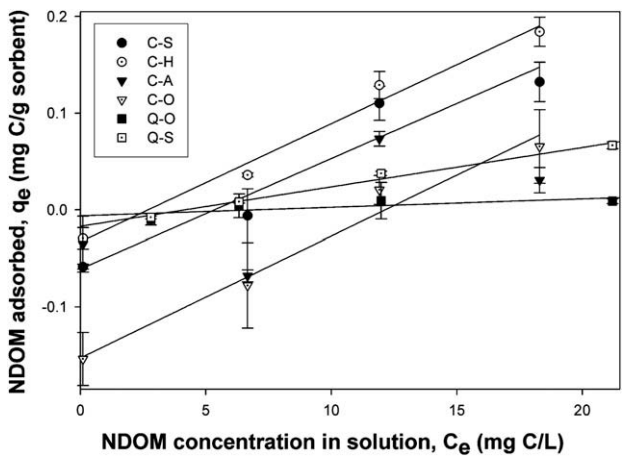

Fig. 3. Adsorption data for NDOM on six carbonate sorbents (C–S, C–H, C–A, C–O, Q–O and Q–S). All sorbents are 0.15–0.5 mm grain size and adsorption time period is 2 days. Error bars represent the standard deviation of duplicate analyses. Solid lines are the linear model adsorption isotherms.

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imental duplicate treatments are in close agreement. It is also clear from plotted isotherms that, unlike the quarry material isotherms with *y*-intercepts close to zero, those of aquifer core materials have negative values, implying the release of indigenous OM. The amount of OM released from the C–O sample (0.1539 mg C/g sorbent) was greatest of all the aquifer sorbents tested. C–S released 0.0584 mg C/g sorbent, while C–H, C–A, Q–O and Q–S released 0.0294, 0.0352, 0.0101 and 0.0080 mg C/g, respectively. Adsorption of NDOM only occurred at background solution concentrations greater than 13 mg C/L.

3.2. NDOM compositional change due to mineral interaction

All the north Florida NDOM (soil, stream and lake) tested were spectra-fluorometrically similar so were likely to have fresh and humified terrestrial vegetation as the common primary source. A representative EEM of soil NDOM (Fig. 4a) shows the location of 4 main fluorophores identified previously by others (Coble, 1996): fulvic-like (C, excitation/emission wavelengths: 295–305 nm/410–420 nm), humic-like (A, 210–260/410–450 nm), and two tryptophan-like fluorophores (T1, 275–280/340–360 nm and T2, 215–220/310–340 nm). EEM graphs of stream and lake NDOM are similar to that of soil extract except that they lack the tryptophan-like fluorophores, which may represent a fresher microbially-derived component (Parlanti et al., 2000). The indigenous OM released from most of the carbonate sorbents (into OC-free DI water) was found to contain humic-like fluorophores, which were also present in sorbate NDOM (core materials, Fig. 4c–f). The difference EEM (emission intensity of background solution before carbonate rock interaction, less that of background solution after

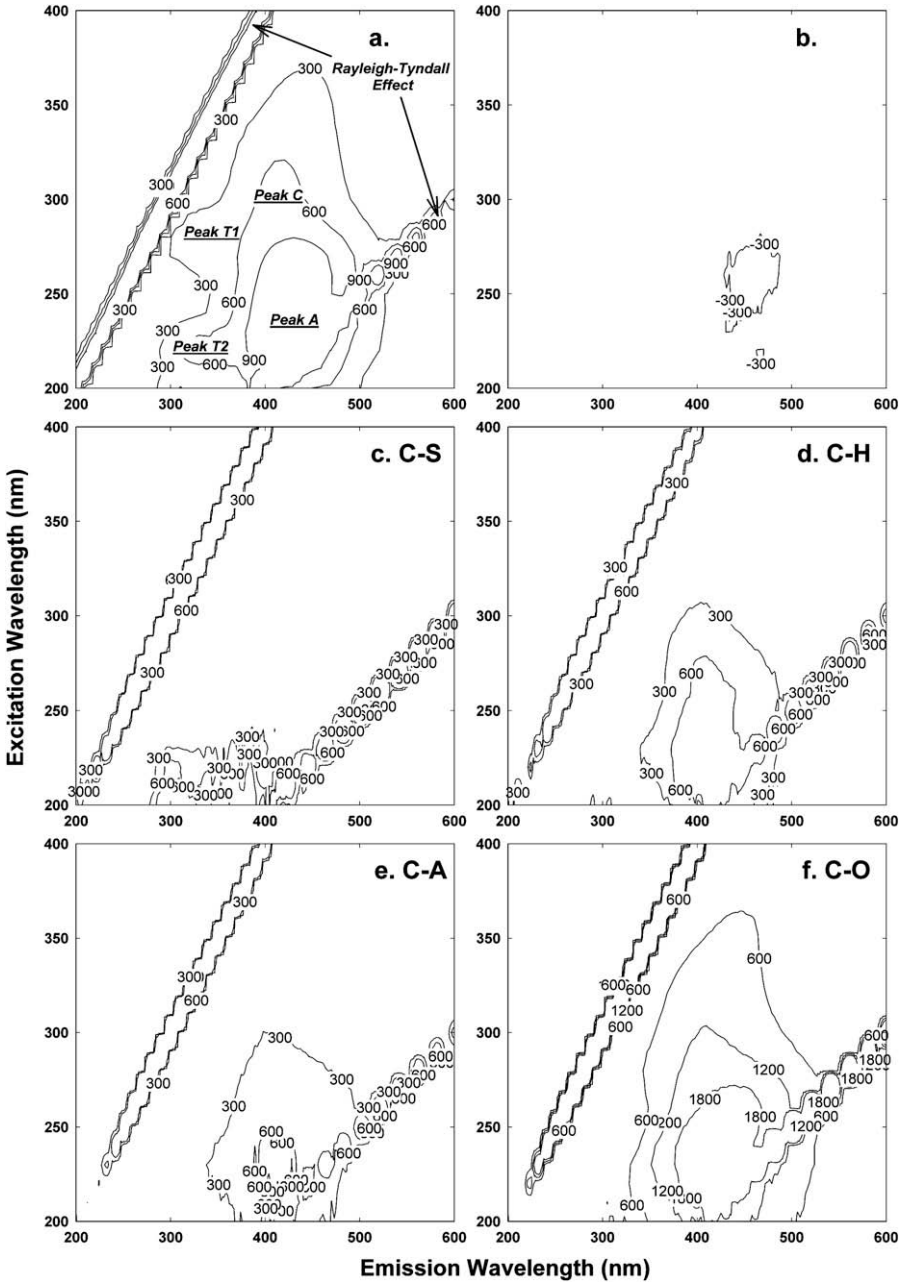

Fig. 4. Excitation–emission matrices (EEM) of (a) soil NDOM extracts with position of fulvic-like (Peak C), humic-like (Peak A), and tryptophan-like (Peaks T1 and T2) fluorophores, (b) difference EEM showing change following 2-day interaction of carbonate rock (C–H, 0.15–0.5 mm) with NDOM (18.19 mg C/L), note that the lower portion of the peak was obstructed by the Rayleigh–Tyndall effect, (c) to (f) EEM of indigenous organic matter released into water from aquifer core materials, C–S, C–H, C–A and C–O, respectively (all <0.15 mm, 2-day interaction).

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interaction), shows the fluorophores that preferentially adsorbed as negative values. Humic-like fluorophores were found to be preferentially adsorbed relative to the other three fluorophores for all aquifer materials (example shown in Fig. 4b). Note, however, that the humic-like fluorophores were partly obstructed by the Rayleigh–Tyndall effect.

All three NDOM (soil, stream and lake) tested displayed identical gaussian M_w distributions in size exclusion chromatograms, with an average peak retention time of 11.7 ± 0.1 min (corresponding to 30.6 ± 1.1 kD in M_w, Fig. 5). Groundwater well samples collected in the Santa Fe River Basin of north Florida were also found to have similar M_w distributions. Further, freeze dry-concentrated and non-concentrated NDOM displayed the same M_w distribution. These findings support the use of freeze dry-concentrated soil NDOM as representative of groundwater NDOM in the region.

Following sorbent interaction, M_w distributions of NDOM decreased (longer peak retention time), indicating preferential adsorption of larger M_w (example in Fig. 5: FGS core materials, 2-day interaction). The preferential adsorption of larger M_w was slightly less for C–A and C–O (1-min increase in retention time, corresponding to 10.9 kD), and slightly larger for C–S and C–H (2-min increase, 21.9 kD). Sorbent size had no effect on the quality of NDOM adsorbed.

Two peaks were found in the chromatograms of indigenous OM via quarry material-DI water blank controls, with average retention time of 11.9 (28.5 kD) and 12.7 min (19.7 kD), respectively. Two more peaks were found in solution of core material-DI water controls: 5.9 (94.1 kD) and 16.2 min (~1 kD), indicating the difference in M_w distribution among indigenous OM of different sorbents and sorbate NDOM (Appendix Table A3).

The concentrations of Ca^{2+} and Mg^{2+} in supernatant solutions after 2-day incubations of NDOM with FGS core material were measured to gauge the influence of NDOM on mineral dissolution. In experimental controls (DI water-sorbent pairs), mineral dissolution, with respect to Ca^{2+} release, was greatest for C–H and least for C–A, on a weight-normalized basis. On a surface area-normalized basis, these trends were just the opposite (Fig. 6). In addition, fine particles (<0.15 mm) released more cations to solution than course particles (0.15–0.5 mm). Mineral dissolution was also detected after interaction with NDOM; however, the amount of cations released from the aquifer materials was less than when in water alone. Further, for both size fractions, the reduction in cation release increased with increasing NDOM concentrations. For example, after a two-day interaction of core materials (0.15–0.5 mm) with NDOM (18.19 mg C/L), release of Mg^{2+} from C–O was inhibited by 82.3%, from C–S by 73.1%, and from C–H and C–A by 38.7% and 44.5%, respectively. The extent of dissolution indicated by Ca^{2+} release was not the same as that indicated by Mg^{2+}.

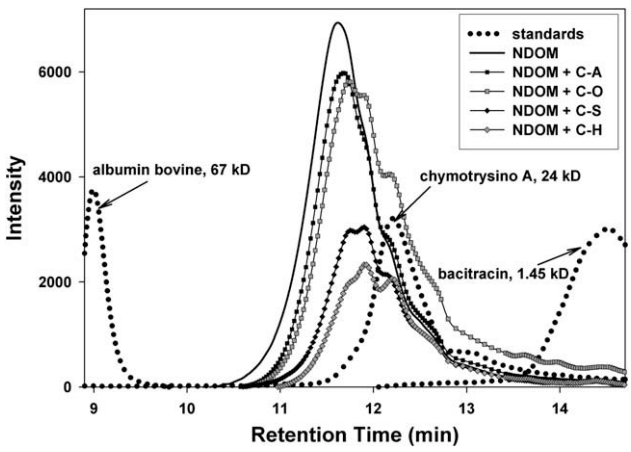

Fig. 5. Liquid size exclusion chromatograph (HPLC-SEC) of NDOM sorbate (14.47 mg C/L) before and after 2-day interaction with 4 aquifer core materials (C–S, C–H, C–A and C–O, all 0.15–0.5 mm). Also shown are 3 protein molecular weight (M_w) standards (bacitracin, M_w = 1.45 kD; chymotrysino A, 24 kD; albumin bovine, 67 kD).

4. Discussion

4.1. Adsorption character and controlling factors

While significant adsorption occurred at most NDOM concentrations for the quarry samples tested, release of indigenous OM from the aquifer core samples occurred at lower NDOM concentrations (<10 mg C/L). At higher NDOM concentrations, core materials displayed an even greater affinity for NDOM than quarry materials. To clarify the contrasting behavior of the carbonate interaction with NDOM at its higher and lower ends of its common natural concentration range, the percentage of NDOM adsorbed at two background concentrations was calculated, based on the derived linear model, for each NDOM–carbonate pair (Table 3). At a NDOM concentration of 5 mg C/L, most of core materials, as well as Q–O, showed negative values in both amount and percentage of NDOM adsorbed, indicating the release of indigenous OM from the sorbents. However, at a higher concentration (e.g., 20 mg C/L), such as might be measured after a major precipitation event when soil OM is flushed into the aquifer, 20–72% of the solution NDOM was adsorbed. Most notable is the linear isotherm which implies that a maximum adsorption capacity is not reached, nor is the NDOM in solution completely adsorbed. A better understanding of the factors producing these trends can be obtained through an examination of the variation in adsorption behavior and controlling factors between each of the samples.

Unlike most previous research that has carried out adsorption experiments using pure mineral sorbents such as metal oxides, calcite, clays etc., and purified or fractionated organic sorbates such as individual compounds or compound classes, the study is distinguished by its use of both heterogeneous sorbents and sorbates. This was done in an effort to obtain empirical data that could be used to predict or explain temporally and spatially distributed field observations of aquifer geochemistry. Elemental and XRD analyses indicate that the carbonate sorbents used in the study contain, in addition to calcite and dolomite (and quartz in the case of Hawthorn Group and Suwannee Limestone materials), variable subdominant amounts of apatite, metal oxides, clay and even OM (Table 1, Appendix Table A1). It is unsurprising, therefore, that the mineralogically more homogeneous quarry materials, Q–O and Q–S, produce highly linear isotherms, while their relatively heterogeneous core material counterparts produce adsorption data with significant scatter. To the contrary, it is in some ways surprising that the combination of heterogeneous sorbents and heterogeneous sorbates produce isotherms with any significant linearity at all. One explanation is that, although isotherms can be considered a combination of several individual isotherms that are characteristic for each specific type of sorbent and sorbate, they mostly reflect the adsorption character of the prevalent sorbate and sorbent pair. In these experiments, that is likely to be humic acids and calcite.

Linear adsorption isotherms, such as observed here for NDOM–carbonate interaction, are commonly explained using partition theory, which applies mainly to the adsorption of nonionic, non-polar and hydrophobic organic compounds via weak, physical forces such as van der Waals attraction (Essington, 2004). Bulk, as opposed to fractioned, NDOM may vary widely in its hydrophobicity, as it commonly contains ionic or polar moieties (e.g., carboxyl and amine groups) coexisting with non-polar ones (e.g., alkyl chains and aromatic rings). However, partition theory is lim-

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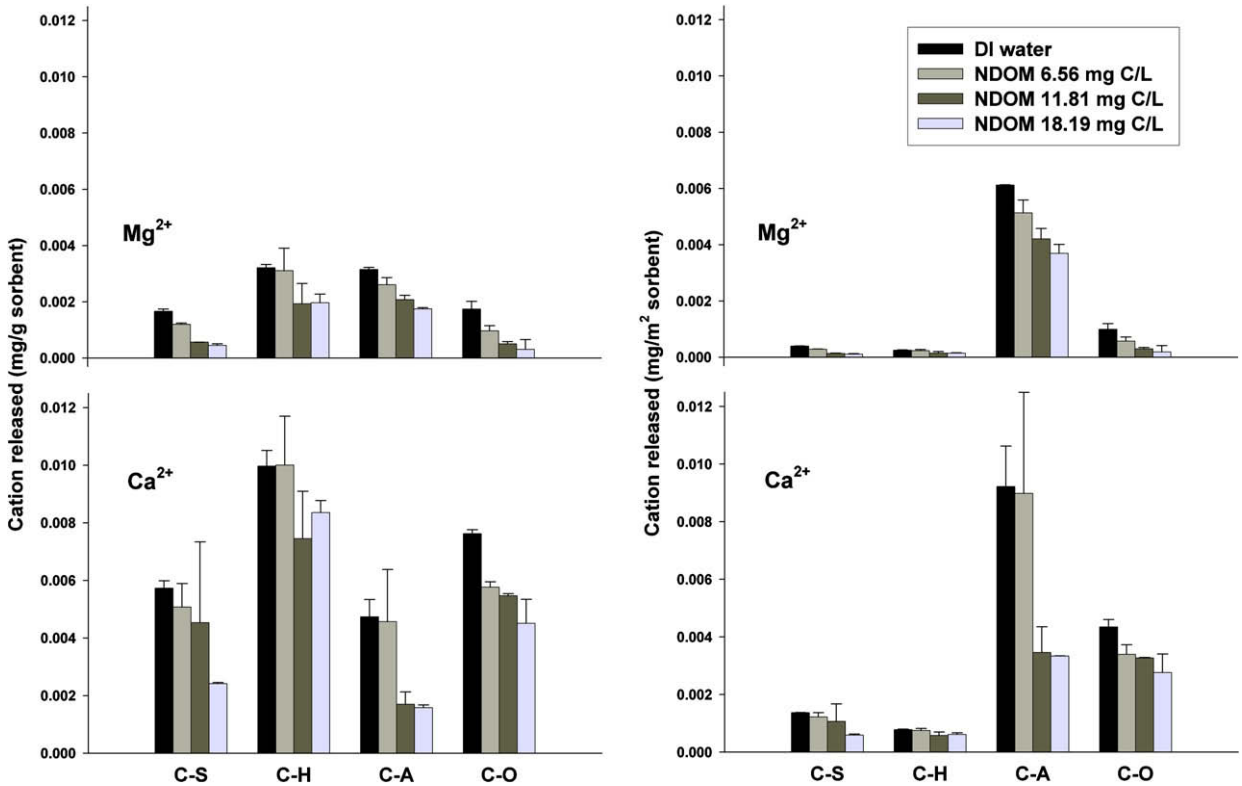

Fig. 6. Ca^{2+} and Mg^{2+} released during 2-day interaction of distilled water and three concentrations of NDOM with aquifer core materials (C–S, C–H, C–A and C–O, all 0.15–0.5 mm). Left: Cations released normalized to sorbent weight (mg/g sorbent). Right: Cations released normalized to sorbent surface area (mg/m^2 sorbent).

Table 3
Amount and percent of NDOM adsorbed at two NDOM solution concentrations for each NDOM–carbonate pair.

Experimental treatment[a]	5 mg C/L		20 mg C/L	
	NDOM adsorbed[b] (mg C/g sorbent)	% NDOM adsorbed	NDOM adsorbed (mg C/g sorbent)	% NDOM adsorbed
Q–S,<0.15 mm, 4-day	0.014	44.1	0.089	67.2
Q–S,<0.15 mm, 2-day	0.013	35.2	0.088	59.7
Q–S, 0.15–0.5 mm, 4-day	0.005	18.6	0.065	59.7
Q–S, 0.15–0.5 mm, 2-day	0.006	28.7	0.051	52.8
Q–O,<0.15 mm, 4-day	0.007	51.0	0.037	64.4
Q–O,<0.15 mm, 2-day	−0.006	−47.6	0.024	34.6
Q–O, 0.15–0.5 mm, 4-day	0.000	−1.3	0.015	50.0
Q–O, 0.15–0.5 mm, 2-day	−0.003	−40.3	0.012	35.3
C–H, 0.15–0.5 mm, 2-day	0.027	38.6	0.207	72.3
C–S, 0.15–0.5 mm, 2-day	−0.006	−5.2	0.159	57.3
C–O, 0.15–0.5 mm, 2-day	−0.088	−122.9	0.107	34.0
C–A, 0.15–0.5 mm, 2-day	−0.025	−31.2	0.050	19.9

[a] Treatment listed as sorbent type, particle size and interaction time period.
[b] Calculated using linear isotherms parameters listed in Table 2. Negative values show release of indigenous OM from the sorbents.

ited in describing the NDOM–carbonate adsorption system because NDOM is composed of a continuum of hydrophobic from hydrophilic compounds. Also, partition theory generally refers to an 'absorption' rather than an 'adsorption' mechanism. The former may be applicable if indigenous OM is the primary sorbent in aquifer materials but not, generally, for minerals without significant microporosity.

Certainly, the physical and chemical property of sorbents is another factor likely to control adsorption. The contrasting character of the quarry materials versus core materials make an interesting comparison with regard to their sorbent behavior. Although somewhat different in chemical composition, the textures of these two sorbent sources are quite different. Core material, being more friable, porous and permeable, is likely to have seen greater groundwater, NDOM and microbial interaction (although subaerial exposure of aquifer materials may also show friable and porous characteristics), resulting in alteration and addition of minor impurities such as secondary minerals, indigenous OM and metal oxides. The core materials may be better representatives of the aquifer materials likely to interact with groundwater, and thus, alter their chemistry.

One might expect mineral surface to exert a dominant control on surficial reactions such as adsorption. However, having very little significant microporosity, none of the aquifer materials displayed large surface areas. The core samples displayed roughly twice the adsorption affinity of their rock counterparts as well as higher surface areas. However, no significant correlation was found between NDOM adsorption affinity (k_D) and the surface area of all

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six carbonate sorbents (R^2 = 0.774, p value of the slope = 0.163) or of the core materials alone (Fig. 7a, R^2 = 0.933, p = 0.543). But, an excellent linear correlation was found between k_D and surface area for the quarry samples alone (Fig. 7a, R^2 = 0.990, p = 0.023) indicating that surface area may be a controlling factor of adsorption for relatively pure carbonate samples, but not when other impurities are present.

Another possible control of adsorption is the presence of indigenous OM in the aquifer sorbents. The polar nature of the surface of most mineral sorbents, including calcite (commonly hydroxyl- and oxy-moieties), will preferentially attract polar substances (e.g., water) over less polar and nonionic NDOM via H-bonding. Adsorption of organic molecules onto carbonate surfaces requires displacing the water molecules at such a surface, which can be thermodynamically unfavorable. However, OM adhering to, or incorporated within, a mineral renders its surface more hydrophobic and will not require the displacement of tightly bound water molecules prior to adsorption of additional OM (Schwarzenbach et al., 2003). Previous studies have found that organic coatings may render hydrophilic surfaces hydrophobic and more capable of sorbing organic contaminants (McCarthy and Zachara, 1989; Murphy et al., 1990). It is expected, therefore, that NDOM will have greater adsorption affinity for sorbents with more indigenous OM. A moderately strong linear correlation was found between the amount of indigenous OM in each sorbent and k_D (Fig. 7b, R^2 = 0.868, p = 0.101). Though only significant to the 90% level of confidence, considering the other known and unknown impurities in the sorbents that could affect this relationship (and surface area as discussed previously), it is reasonable to conclude that the presence of indigenous OM strongly influences NDOM adsorption.

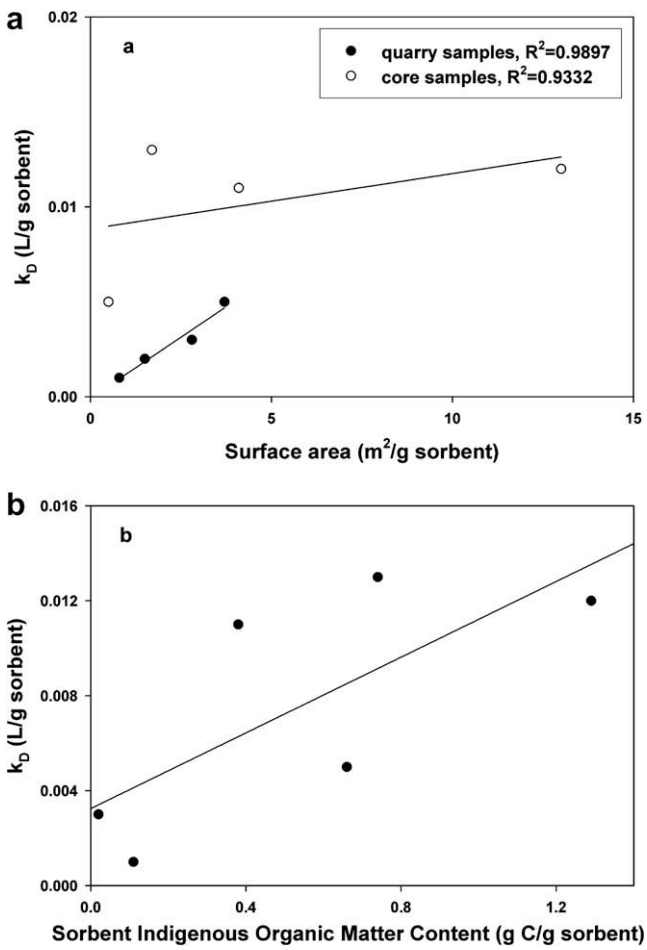

Fig. 7. Plots of adsorption affinity (k_D: L/g sorbent) versus (a) sorbent surface area (m^2/g sorbent) and (b) sorbent indigenous organic matter content (g C/g sorbent) for different Floridan Aquifer materials.

4.2. Adsorption kinetics and mechanism

Irreversible adsorption of humic acid to calcite, as well as to metal oxide has been attributed to ligand exchange and inner-sphere-like interactions (Gu et al., 1994; Lee et al., 2005; Murphy et al., 1990). However, for environmental processes, it is perhaps inappropriate to model adsorption reactions as either completely reversible or completely irreversible. It has been suggested that the adsorption is kinetically biphasic, made up of a rapid and reversible initial stage and followed by a much slower nonreversible stage (Selim et al., 1992; Vaccari and Kaouris, 1988). The formation of inner-sphere surface complexes and bonds of a covalent character are commonly believed to occur during the slow phase (Gu et al., 1994), whereas, the authors posit that the bonds formed during the 2 and 4-day experiments conducted in the present study are mainly weaker outer-sphere interactions of the rapid initial phase.

Because the carbonate sorbents exhibited greater NDOM adsorption after 4 versus 2 days, it can be concluded that adsorption equilibrium was not achieved. For instance, with a 5 mg C/L background NDOM concentration, Q–S (<0.15 mm) showed an increase of 8.9% in NDOM adsorption after 4-relative to 2-days, and there was a 14.7% increase for Q–O at 20 mg C/L (Table 3). The increase was most apparent at higher NDOM concentration (>60 mg C/L) than likely to be found in aquifers. By comparison, a previous study reported SRHA adsorption to calcite to be rapid, reaching equilibrium within one day (Lee et al., 2005). In contrast, the non-equilibrium found in the present study may reflect the heterogeneity of both sorbents and sorbates. That is, carbonate rocks with a variety of minerals and surface functional groups may bind by a variety of mechanisms (rapid and slow forming) to a complex NDOM mixture. It was reported that no sorption equilibrium was reached in a system of phenanthrene and aquifer materials during adsorption experiments lasting 1010 days (Rugner et al., 1999). The transport of organic components in groundwater was shown to display non-equilibrium features due to very slow sorption kinetics onto aquifer materials or soils (Curtis et al., 1986; Pignatello et al., 1993; Roberts et al., 1986). In some cases, the slow sorption was attributed to intraparticle pore diffusion (Ball and Roberts, 1991; Grathwohl and Reinhard, 1993; Werth et al., 2000), and in another case, to a high sorption capacity (Kleineidam et al., 2004).

Assuming the studied carbonate system has a maximal adsorption capacity, though not observed, and considering the fact that adsorption of hydrophilic components can produce nonlinear adsorption behavior, it is likely that the linear isotherms observed in the study are only the low-concentration portion of a Freundlich or Langmuir isotherm with an adsorption capacity much higher than the natural NDOM concentration range. In this case, adsorption sites on carbonate minerals are far from being saturated at low NDOM concentrations. However, at much higher NDOM concentrations, adsorption would become more and more difficult until all the sites are occupied (when k_D = 0). Murphy et al. (1990) reported that different isotherm models apply to different sorbate concentration ranges. For example, Lee et al. (2005) found that a SRHA-calcite adsorption system showed Langmuir adsorption isotherm behavior at low concentrations (0–15 mg C/L) and non-Langmuir behavior at higher concentrations.

During the desorption experiment stage, when background NDOM solution concentration was lowered, most, but not all of the adsorbed NDOM was released (e.g., 73–88% adsorbed OC was desorbed by C–S). One sign that desorption equilibrium occurred

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is the near equivalence of the desorption and adsorption k_D, or isotherm slope (Essington, 2004). In addition, the preferential adsorption of hydrophobic NDOM (discussed below), which is often not completely reversible could have caused the hysteresis. However, factors other than true irreversible adsorption can cause this hysteresis, such as experimental artifacts, inappropriate experimental design, and non-equilibrium of either the adsorption or desorption process. Given that the adsorption was apparently not at equilibrium and that the appearance of hysteresis might be created by releasing additional OM into the low-concentration solution during desorption stage, it is likely that the hysteresis observed was a false one.

Observations, by some, of the preferential adsorption of acidic organic compounds and an accompanying pH increase in background solution has led to the proposal that ligand exchange is the predominant adsorption mechanism of OM onto calcite (Carter, 1978) and Fe oxide (Tipping, 1981). Ligand exchange is not likely the primary adsorption mechanism occurring in the present system, as no pH change was detected. However, considering that the carbonate minerals provide a strong pH buffer, the change in pH reflecting the extent of ligand exchange might have been too small to be detected. Structural changes in the orientation of certain NDOM functional groups (e.g., –COOH and –OH) during hydrophobic interaction between NDOM and sorbents might also explain the small change in acidity during adsorption (Avena and Koopal, 1999; Davis, 1982; Geffroy et al., 2000).

It is proposed that the NDOM–carbonate adsorption process consisted of a rapid and reversible initial stage, followed by a slower irreversible stage. During the rapid initial stage, weak and outer-sphere bonding is the main association between carbonate sorbents and sorbed organic molecules. At longer time intervals, the stronger hydrophobic interactions occur, transforming the carbonate surface from hydrophilic to hydrophobic and facilitating further hydrophobic interactions.

4.3. Consequences of abiotic NDOM–carbonate interaction

4.3.1. NDOM transformation

The observation of preferential adsorption of humic-like over fulvic-like and high over low M_w NDOM (Figs. 4b and 5, respectively) onto carbonate sorbents is consistent with the findings of other published studies. For example, higher M_w and more hydrophobic organic compounds were found to be preferentially adsorbed, relative to lower M_w and hydrophilic fractions, to both clay and metal oxide sorbents (Gu et al., 1994; Hur and Schlautman, 2003; Meier et al., 1999). Hydrophobic constituents of naturally occurring organic matter were preferentially adsorbed in laboratory columns containing well-packed aquifer material (Dunnivant et al., 1992). It was hypothesized that hydrophobic effects, followed by a ligand exchange, were the dominant mechanisms contributing to the preferential adsorption of lower over higher M_w components of SRHA onto a synthetic aquifer material (Chi and Amy, 2004). Zullig and Morse (1988) concluded that fatty acids with relatively longer C chains preferentially adsorb to calcite surfaces due to the 'hydrophobic effect'. Therefore, the aromaticity of NDOM in carbonate aquifer systems is likely to be an important determinant of the NDOM adsorption and groundwaters enriched in fulvic acids and low M_w components may be recognized as post-mineral interaction or 'aged'.

The indigenous OM detected in the aquifer materials may influence the adsorption process by altering both NDOM composition and sorbent surface chemistry. Indigenous OM released from the carbonate sorbents was most apparent at low NDOM solution concentrations and among the core sorbent materials with little OM release from the low OC quarry materials. However, no significant linear correlation was found between the amount of indigenous OM released and measured sorbent OC content in each sample. For example, C–H, with the highest OC content among the 4 core materials, had the weakest tendency to release OM into solution, while C–O released the most OC. It may be that the type of indigenous OM and its influence on NDOM adsorption differs among aquifer formations. Other sorbent chemical parameters such as surface area, elemental composition, adsorption affinity, and cations released to solution were also not found to be significantly related to OM release. It is surmised that indigenous OM in these samples may be heterogeneously distributed in aquifer material and may be present as inter-particle inclusions as well as crystal surface coatings.

The possibility of exchange of sorbate NDOM for indigenous OM must also be considered, and for this, OM compositional indicators can be useful. EEM showed that indigenous OM released from carbonate samples generally contained humic-like substances (peak A), except for C–O, which released the most OC, which contained both humic-like and fulvic-like substances (Fig. 4c–f). In addition, HPLC-SEC M_w distributions showed indigenous OM of both core and quarry materials to be composed of two common peaks (average M_w = 28.5 and 19.7 kD), and two additional peaks in core materials (average M_w = 94.1 and about 1 kD), distinct from the NDOM peaks (average M_w = 30.6 kD). Thus, the indigenous OM found within these quarry materials is composed of humic-like substances (similar to that found in soil, stream and lake NDOM) as well as both large and small M_w compounds that can be more released when background NDOM concentrations are low. This release of indigenous OM may occur particularly when carbonate surfaces are exposed due to dissolution. Further, the direct observation of these indigenous OM peaks (HPLC data) in the post-interacted background solution confirms the exchange of OM between the aqueous and solid phases. The origin of the indigenous OM is not known, but, besides previously sorbed humic substances, it may include microbially-derived degradation products. It follows that some of this material is relatively more labile than the infiltrating NDOM for which it is exchanged on mineral surfaces and, may, therefore, fuel subsurface microbial activity.

4.3.2. Carbonate dissolution

Though microbial conversion of OC to inorganic C should increase the rate of carbonate dissolution (Perry et al., 2003, 2004), it is likely this effect was small to absent in the experiment because the samples were treated aseptically and the 2-day interaction period allowed little time for acclimatization of any microbes to the OC source. Thus, release of Ca^{2+} and Mg^{2+} cations into solution can be attributed to abiotic hydrolyzation of mineral surfaces.

On a weight-normalized basis, C–H had the greatest dissolution tendency and C–A the least. However, on a surface area-normalized basis the trend was just the opposite. This may be because the higher surface area of C–H is due to clays which did not release cations. Although surface area may be a contributing factor in determining dissolution extent, mineralogy played a more important role. For example, dolomite, the main constituent of C–A, has a much lower solubility product than calcite, the dominant mineral of the other three core materials (at 25 °C, $K_{calcite} = 10^{-8.48}$, $K_{dolomite} = 10^{-17.2}$, Drever, 2002) and released least Ca^{2+} on a weight-normalized basis. C–S showed lower Mg^{2+} and Ca^{2+} release than C–O, likely due to the presence of quartz which lowered its calcite content. Though it contains significant quartz, the relatively high cation release from C–H, may be due to its apatite which has a high solubility.

In general, the presence of NDOM inhibited mineral dissolution, but the dissolution inhibition observed was not always proportional to NDOM solution concentration. For example, little inhibition occurred at 6.6 mg C/L NDOM, the concentration at which little NDOM adsorption occurred. There was only a small difference

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in extent of inhibition and NDOM adsorption at 11.8 versus 18.2 mg C/L NDOM. These observations suggest that the inhibition of mineral dissolution due to protection of mineral surface by organic coating may have a minimum threshold of coverage (extent of thickness) at which it becomes effective.

Though the issue of whether OM inhibits or enhances carbonate dissolution is still debated, the findings are in agreement with a number of previous studies. Thomas et al. (1993) reported that organic compounds strongly sorbed to calcite and dolomite inhibited dissolution, while weak sorbates and non-sorbates showed little or no effect on dissolution rates. In addition, the asynchronous dissolution inhibition evident from the different release rates of Ca^{2+} and Mg^{2+} suggests that NDOM does not inhibit the dissolution of all minerals equally. For example, because Mg^{2+} release was more inhibited by the presence of NDOM than Ca^{2+} release in all cases, Mg^{2+}-containing minerals such as dolomite may be relatively more protected by NDOM coverage. However, one must note that while these experiments were carried out in DI water (with zero ionic strength) native groundwater may have low to relatively high ionic strength, depending on its source. In native groundwater solutions, less carbonate dissolution would be expected to occur due to higher Ca^{2+} and Mg^{2+} concentrations, but more could occur in solutions with higher dissolved CO_2 concentrations.

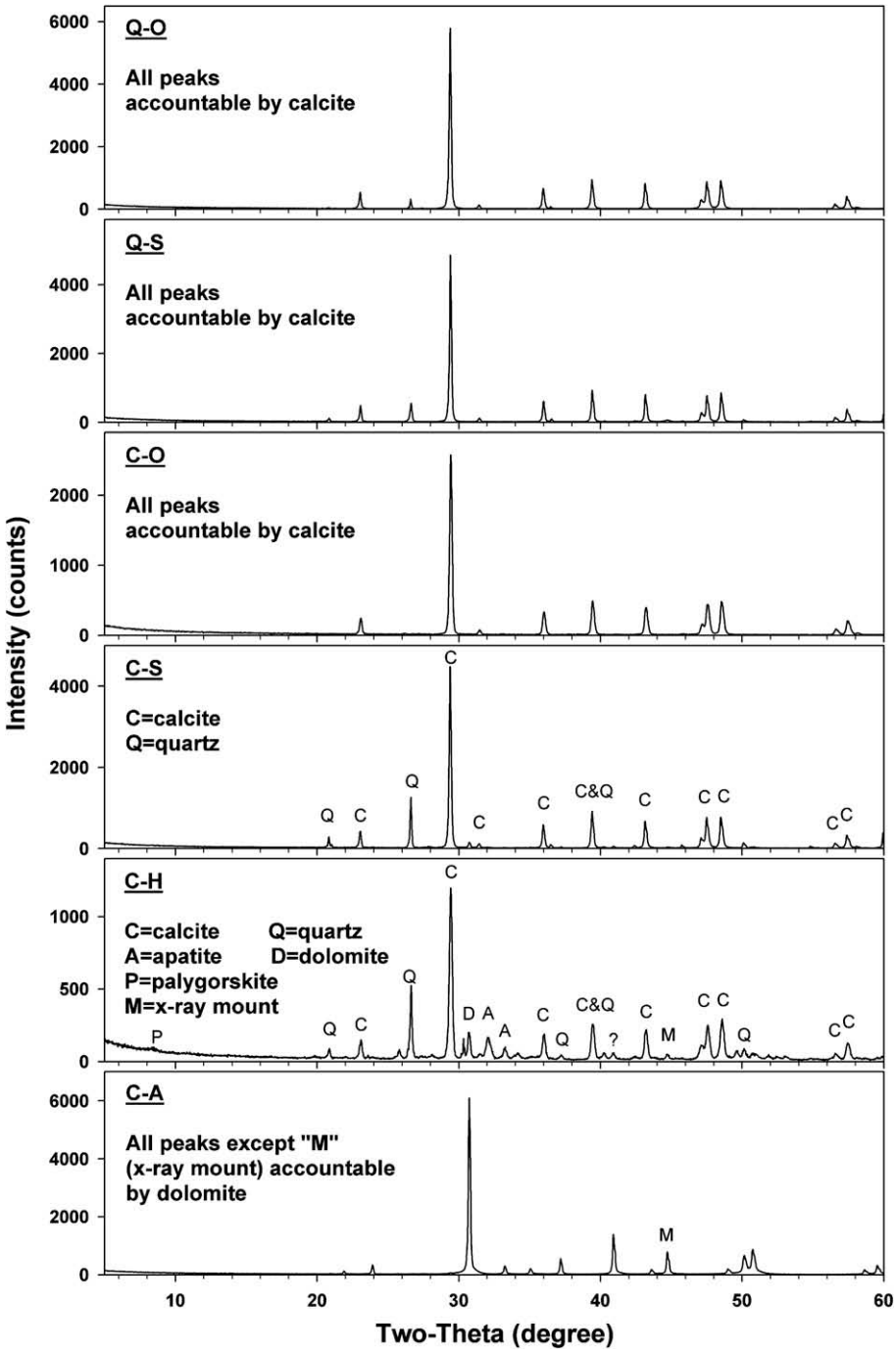

Fig. A1. Sorbent X-ray diffraction results. XRD results show that the Q–O, Q–S, C–O are nearly pure calcite, the C–A is nearly pure dolomite, C–H has calcite, dolomite, quartz, apatite, and palygorskite, and C–S is calcite and quartz.

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5. Conclusions and Implications

The hydrogeology of an aquifer plays a role in the subsurface fate and transport of organic pollutants and natural OM. Factors such as depth to water table, sediment porosity and permeability, grain size and mineralogy of aquifer material, and groundwater flow velocity all control the pace and extent of OM consumption and transformation both spatially and temporally. While it is well known that microbial utilization will alter the amount and character of NDOM along its subsurface flow path and alter redox conditions that control the release of potentially harmful metals and radio-nuclides, the results presented here for carbonate aquifer systems make clear the important role that abiotic factors can potentially play as well, primarily by governing the supply of OM to the microbes. Given the relatively greater surface connectivity and permeability, and thus, variability in NDOM concentration and contact time in these systems, the effects of abiotic interaction of NDOM and carbonate are likely to be temporally and spatially variable. The results of this study show that, due to slow adsorption kinetics, longer groundwater retention or slower flow rates will lead to greater NDOM adsorption in a carbonate aquifer. At lower NDOM concentrations, such as during dry periods or at locations distant from NDOM sources, OM may be released from carbonate rock. In contrast, at greater NDOM concentrations, such as following rain events or at locations close to NDOM sources, considerable NDOM sequestration may occur via carbonate interaction.

The preferential adsorption of humic-like NDOM to carbonate materials will alter groundwater quality rendering it more hydrophilic. Those OM components that are not adsorbed may be considered the more likely fuel for microbial metabolism and may be of greater concern in terms of drinking water quality (for more hydrophilic anthropogenic organic contaminants). The fate and transport of environmentally damaging nutrients such as nitrates and phosphates, too, may be tied to that of NDOM. For instance, if the amount of degradable OM exceeds the available dissolved O_2, which is common in groundwater systems, then the aquifer may become denitrifying if NO_3 is available as an electron acceptor (National Research Council, 2008). The results also suggest that adsorption of NDOM to aquifer materials can also remove the more hydrophobic organic N and P and prevent their possible remineralization by microbes. In contrast, NDOM released by carbonate can serve as an electron acceptor and stimulate the conversion of N and P into microbial biomass.

The finding that the dissolution of Floridan Aquifer carbonate aquifer materials of all types examined is inhibited by the presence of NDOM at all concentrations has environmental implications as well. However, biotic processes must also be considered such as the release of inorganic C by microbial mineralization of NDOM which will enhance carbonate dissolution. The relative influence of abiotic and biotic factors on carbonate dissolution will also be important to determine in areas such as karst where land surface subsidence may occur.

This improved understanding of the abiotic NDOM–carbonate interaction processes which may occur in carbonate aquifer systems will be of benefit when conducting hydrogeologic projects such as ASR and aquifer recharge (AR). For example, a project manager may want to consider whether a pretreatment removal of NDOM prior to subsurface injection may ultimately be of benefit or harm, both from an environmental and from a groundwater quality point of view. While it is understood that caution is required when conducting projects such as ASR using water that contains NDOM, the present study suggests that NDOM removal may also have implications of environmental consequences such as enhanced karstic dissolution. Clearly additional work should be carried out to examine both abiotic and biotic NDOM–mineral interactions simultaneously, such as in incubations using native groundwater microbial populations. These experiments should be carried out in both batch and column modes. Lastly, field-scale 'ground-truthing' studies need to be conducted in well-monitored systems. The initiation of both ASR and AR projects in Florida afford just such an opportunity to examine the effects of NDOM interaction on subsurface biogeochemical processes (National Research Council, 2008).

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Appendix A

See Fig. A1 and Tables A1–A3.

Table A1
Background information on Upper Floridan Aquifer sorbents used in this study.

Sample code	Location	Sample information/core depth	Major elemental composition (weight %)[c]											
			SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	CO_2	S	S (SO_4)
Core samples[a]														
C–H	Palm Beach County, FL	W-18728; 242.9–243.2 m (797–798 ft)	17.7	1.9	0.3	3.2	38.9	0.7	0.5	0.1	6.4	25.7	0.4	1.1
C–S	Collier County, FL	W-17801; 296.9–297.2 m 974–975 ft)	15.3	0.6	0.1	0.5	45.6	0.2	0.2	bdl	0.3	34.4	0.1	0.1
C–O	Hendry County, FL	W-18720; 362.7–363.0 m (1190–1191 ft)	0.5	0.2	bdl[d]	0.9	53.1	0.1	0.1	bdl	bdl	41.8	0.3	0.3
C–A	Osceola County, FL	W-18725; 298.7–300.2m980–985 ft	0.7	0.2	0.1	18.5	32.8	0.1	0.1	bdl	bdl	40.5	bdl	0.5
Quarry samples[b]														
Q–S	Brooksville, FL	Quarried	Not determined											
Q–O	Newberry, FL	Quarried	Not determined											

[a] Core samples provided by the Florida Geological Survey (FGS), Tallahassee, FL.
[b] Quarry samples provided by Florida Department of Transportation (FDOT), Tallahassee, FL.
[c] Major elemental composition data (in weight %) of sorbents provided by Florida Geological Survey, Tallahassee.
[d] Below detection limits.

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Table A2
Alternative adsorption model parameters (weight-normalized adsorption).

Experimental treatment[a]	Langmuir model $\left(q_e = \frac{q_{\max} K_L C_e}{1+K_L C_e}\right)$ parameters			Freundlich model $(q_e = K_F C_e^n)$ parameter		
	K_L (L/mg)	$q_{\max}$ (mg/g)	R^2	K_F (L/g)	n	R^2
Q–S < 0.15 mm, 4-day	1.041E−08	5.126E+05	0.999	0.004	1.063	0.999
Q–S < 0.15 mm, 2-day	1.661E−08	2.948E+05	0.997	0.003	1.098	0.999
Q–S 0.15–0.5 mm, 4-day	1.159E−08	3.446E+05	0.995	0.002	1.150	0.999
Q–S 0.15–0.5 mm, 2-day	1.702E−08	1.968E+05	0.997	0.002	1.095	0.999
Q–O < 0.15 mm, 4-day	4.703E−08	4.295E+04	0.994	0.001	1.077	0.995
Q–O < 0.15 mm, 2-day	3.446E−08	5.007E+04	0.994	0.001	1.141	0.998
Q–O 0.15–0.5 mm, 4-day	4.994E−08	1.955E+04	0.996	0.001	1.082	0.997
Q–O 0.15–0.5 mm, 2-day	6.960E−08	1.183E+04	0.989	0.000	1.170	0.994
C–H 0.15–0.5 mm, 2-day	1.779E−03	6.958E+00	0.994	0.012	1.013	0.994
C–S 0.15–0.5 mm, 2-day	9.843E−03	1.323E+00	0.973	0.013	0.950	0.972
C–O 0.15–0.5 mm, 2-day	1.227E−02	1.236E+00	0.993	0.017	0.900	0.992
C–A 0.15–0.5 mm, 2-day	1.769E−07	2.498E+04	0.583	0.002	1.313	0.592

[a] Treatment listed as sorbent type, particle size and interaction period.

Table A3
Retention time (min) of indigenous organic matter released from Floridan Aquifer materials: peaks detected by size exclusion liquid chromatography.

Sorbent name	Peak 1	Peak 2	Peak 3	Peak 4
Q–O	–	11.8	12.8	–
Q–S	–	11.9	12.6	–
C–H	5.9	11.9	12.8	16.2
C–S	5.9	11.9	12.8	16.2
C–O	5.8	11.9	12.6	16.2
C–A	5.9	11.9	12.6	16.2

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