

# The removal kinetics of dissolved organic matter and the optical clarity of groundwater

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**Abstract** Concentrations of dissolved organic matter (DOM) and ultraviolet/visible light absorbance decrease systematically as groundwater moves through the unsaturated zones overlying aquifers and along flowpaths within aquifers. These changes occur over distances of tens of meters (m) implying rapid removal kinetics of the chromophoric DOM that imparts color to groundwater. A one-compartment input-output model was used to derive a differential equation describing the removal of DOM from the dissolved phase due to the combined effects of biodegradation and sorption. The general solution to the equation was parameterized using a 2-year record of dissolved organic carbon (DOC) concentration changes in groundwater at a long-term observation well. Estimated rates of DOC loss were rapid and ranged from 0.093 to 0.21 micromoles per liter per day ( $\mu\text{M d}^{-1}$ ), and rate constants for DOC removal ranged from 0.0021 to 0.011 per day ( $\text{d}^{-1}$ ). Applying these removal rate constants to an advective-dispersion model illustrates substantial depletion of DOC over flow-path distances of 200 m or less and in timeframes of 2 years or less. These results explain the low to moderate DOC concentrations (20–75  $\mu\text{M}$ ; 0.26–1  $\text{mg L}^{-1}$ ) and ultraviolet absorption coefficient values ( $a_{254} < 5 \text{ m}^{-1}$ ) observed in groundwater produced from 59 wells tapping eight different aquifer systems of the United States. The nearly uniform optical clarity of groundwater, therefore, results from similarly rapid DOM-removal kinetics exhibited by geologically and hydrologically dissimilar aquifers.

**Keywords** Hydrochemistry · Dissolved organic carbon · Reaction kinetics · USA

## Introduction

Among the most remarkable and valued properties of groundwater, and the spring waters derived from groundwater systems, is their striking optical clarity (Davies-Colley and Smith 1995). This clarity, and thus the perceived healthfulness of groundwater relative to many surface waters, has had a profound effect on the history of human water use. Many of the mythologies that have traditionally surrounded groundwater (Bord and Bord 1985) can be traced directly to its clarity relative to most surface waters. More recently, the bottled water industry in the United States was founded in the 19th century on the perception that optically clear spring waters were healthier than municipal water supplies derived from surface-water sources (Chapelle 2005). Finally, the earliest scientific studies of groundwater geochemistry can be traced directly to curiosity about the chemical and optical purity of spring waters (Back et al. 1995). Surprisingly, however, the fundamental hydrologic and geochemical processes that lead to the nearly uniform optical clarity of groundwater are not widely understood.

Although groundwater that has visible color does occur (Tan and Sudak 1992; McConnell and Hacke 1993) it is relatively rare. Much of the color associated with natural groundwater and surface water is due to the presence of dissolved organic matter (DOM), some fraction of which absorbs ultraviolet (UV) and visible (V) light thereby conferring color. This color-producing DOM is referred to as chromophoric dissolved organic matter or CDOM (Blough and Del Vecchio 2002; Fichot and Benner 2011). The lack of color in groundwater compared to many surface waters is largely due to the relative absence of CDOM. However, if one considers that

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CDOM-laden surface waters are the principal sources of recharge to most groundwater systems (DeSimone et al. 2014), it is not intuitively obvious that groundwater should exhibit such near-universal lack of color.

For example, surface water from the black-water Withlacoochee River in southern Georgia, with a median total organic carbon (TOC) concentration of 1,200 micromoles per liter ( $\mu\text{M}$ ); 16 milligrams per liter ( $\text{mg L}^{-1}$ ) and median color of 110 potassium-cobalt units (PCU), drains directly into the karstic Floridan aquifer via sinkholes in the river channel (McConnell and Hacke 1993). Within 200 meters (m) of the recharge zone, TOC concentrations in groundwater decline to less than 300  $\mu\text{M}$  ( $3.9 \text{ mg L}^{-1}$ ) and the color decreases proportionally. By the time the “plume” of river-derived water has been transported 10 km downgradient, the color disappears completely ( $<1$  PCU). This shows that the Floridan aquifer has a substantial capacity to attenuate CDOM concentrations, a characteristic that could explain the striking clarity (PCU $\sim$ 0) of many spring waters derived from the Floridan aquifer such as Silver Springs (Schmidt 2001). In addition, this raises the possibility that other groundwater systems have similar CDOM-attenuating properties.

The dynamics of DOM moving through soils are important in regulating the transport of carbon, and thus energy, within terrestrial ecosystems and have been the subject of extensive study (Neff and Asner 2001). These studies have shown that biodegradation and sorption combine to remove DOM from groundwater circulating through soils and aquifer sediments (Neff and Asner 2001; Kalbitz et al. 2003; Findlay and Sobczak 1996; Baker et al. 2000; Shen et al. 2015). The water-purifying properties of sandy soils have been known for centuries, and were the underlying technology for the famous filter-cisterns in use in Venice, Italy since the first millennia BCE (Chapelle 2005). More recently, engineered artificial recharge systems have been used to remove DOM from recycled treated wastewaters (Rauch and Drewes 2005; Grünheid et al. 2005). Curiously, however, the more universal issue of DOM- and CDOM-removal processes from the soil and surface waters that naturally recharge regional aquifer systems, and their impact on the optical clarity of groundwater, has received less attention.

The purpose of this paper is to develop a method to quantify the removal kinetics of DOM in groundwater using data from a long-term monitoring well. These DOM removal kinetics are then used to provide a quantitative explanation for the uniform clarity of groundwater produced from 59 observation wells tapping eight hydrologically diverse aquifer systems of the United States.

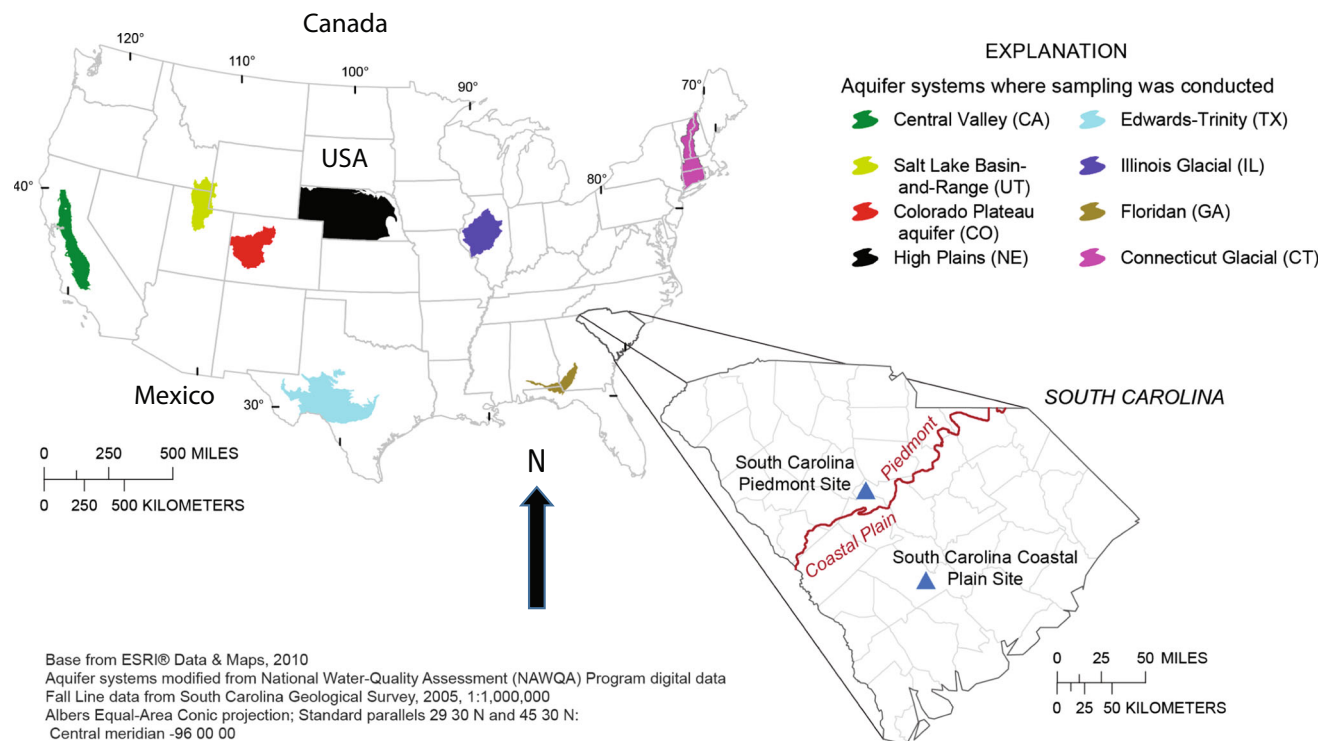
## Materials and methods

Groundwater samples for measurement of dissolved organic carbon (DOC) and UV/V absorbance were collected

according to standard methods (USGS 2006a, b) by teams of the National Water Quality Assessment (NAWQA) program of the US Geological Survey. Samples were collected and analyzed from observation wells completed in ten different aquifer systems of the United States USGS, 2006. These aquifer systems (Fig. 1) include the Piedmont and Blue Ridge crystalline-rock aquifer system of South Carolina (SC Piedmont in Fig. 1;  $n=8$ ), the surficial aquifer system of the South Carolina coastal plain aquifer (SC Coastal Plain in Fig. 1;  $n=30$ ), the High Plains aquifer system of Nebraska ( $n=12$ ), the Colorado Plateau aquifer system of Colorado ( $n=5$ ), the Basin-and-Range aquifer system of Salt Lake City, Utah (Salt Lake;  $n=8$ ), the Floridan aquifer system of Georgia ( $n=5$ ), the glacial sand-and-gravel aquifer system of Illinois (Illinois;  $n=3$ ), the glacial sand-and-gravel aquifer system of Connecticut ( $n=5$ ), the Edwards-Trinity aquifer system of Texas ( $n=19$ ), and the Central Valley aquifer system of California ( $n=6$ ; USGS 2016). These aquifer systems were chosen because of their variety of lithologic, climatic, and hydrologic properties.

The SC Piedmont (Shen et al. 2015), SC Coastal plain (Chapelle et al. 2011), Floridan, Illinois, and Connecticut aquifer systems are characterized by humid climatic conditions and relatively rapid recharge rates. The California Central Valley, High Plains, Salt Lake, and Colorado Plateau aquifers are characterized by more arid conditions and lower recharge rates. The Floridan and Edwards-Trinity aquifers are karstic carbonate-rock aquifers, the SC Piedmont is a fractured metamorphic rock aquifer, whereas the others are clastic aquifers of sedimentary origin. The Connecticut and Illinois aquifer systems are predominantly of glacial origin, and the Central Valley, High Plains, the SC Coastal Plain, Colorado Plateau, and Salt Lake aquifers are largely fluvial in origin. The aquifer systems included in this study, therefore, represent a wide variety of geologic and hydrologic conditions.

A single long-term USGS monitoring well in the SC Piedmont (Shen et al. 2015) was used to study variations in DOC concentrations and UV absorbance in groundwater over time. The location of the SC Piedmont site is shown in Fig. 1. This well is part of the South Carolina Climate Response Network (Station 340837081173800; Name RIC- 748) and is located in a forested area of Richland County (Fig. 1). Groundwater samples for DOC analysis were collected at approximately monthly intervals ( $n=24$ ) between 2010 and 2012 as previously described (Shen et al. 2015). In addition, concentrations of dissolved oxygen (DO) were measured for each sampling event in the field using the Rhodazine D<sup>TM</sup> method for low-range ( $<1 \text{ mg L}^{-1}$ ) concentrations of DO (CHEMetrics Inc 2016). Field measurements for temperature, specific conductivity, and pH were made for each sampling event with a YSI model 556 multi-parameter water-quality sonde (YSI Inc 2016). Concentrations of dissolved iron (Hach 2015a) and sulfide (Hach 2015b) were measured periodically.



**Fig. 1** Locations of the South Carolina (SC) Piedmont and SC Coastal Plain sites and locations of the eight aquifer systems sampled for this study. US states: *CA* California, *UT* Utah, *CO* Colorado, *NE* Nebraska, *TX* Texas, *IL* Illinois, *GA* Georgia, *CT* Connecticut

Samples for DOC analysis were collected in combusted amber glass bottles, kept in the dark at 4 °C, and processed in the laboratory within 72 h of collection. Samples were filtered through pre-cleaned 0.2- $\mu\text{m}$  pore-size membrane filters (Supor®-200, Life Sciences) prior to optical and chemical analyses. Concentrations of DOC were measured using high-temperature combustion via a Shimadzu TOC-V analyzer (Benner and Strom 1993). Milli-Q UV-Plus water was injected every 6th sample as a blank and the blanks were negligible. Absorbance spectra (200–800 nm) of water samples were determined using a dual-beam Shimadzu 1601 spectrophotometer and 10-cm quartz cuvettes. For high-absorbance samples, 1-cm quartz cuvettes were used. Absorbances were corrected for blank (the average absorbance between 690 and 700 nm) and were converted to Napierian absorption coefficients  $a_\lambda$  ( $\text{m}^{-1}$ ) according to the equation:

$$a_\lambda = 2.303A_\lambda/r \quad (1)$$

Where  $A_\lambda$  is the absorbance measured across pathlength  $r$  at a wavelength  $\lambda$  (254 nm). The time-series DOC concentrations at the USGS observation well have been previously published by Shen et al. (2015).

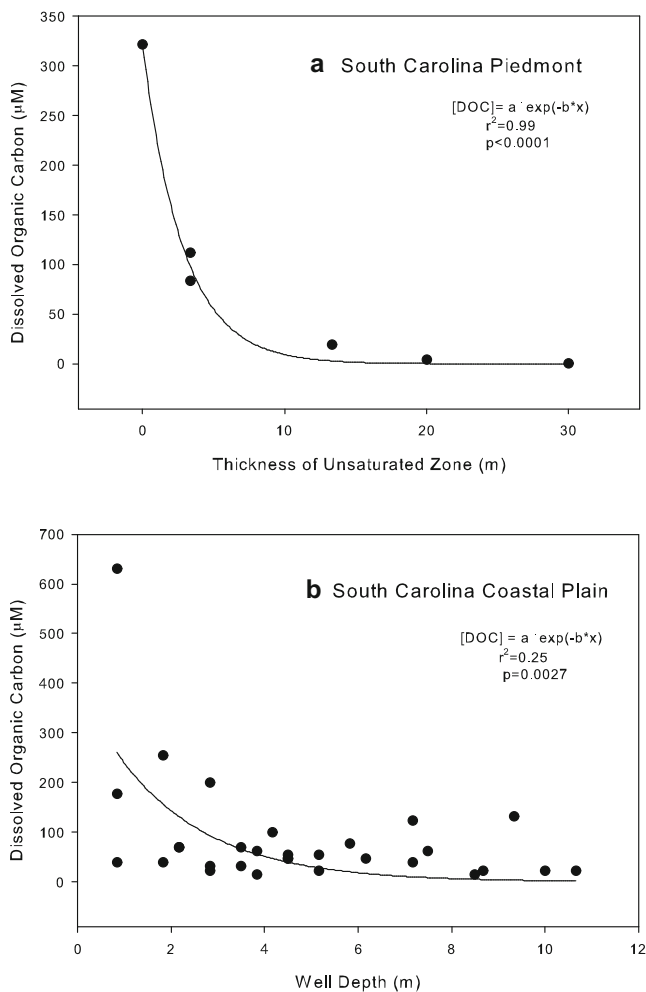
Regression analyses were used to compute a DOC/ $a_{254}$  evolution pathway for SC Piedmont and Coastal Plain samples, and to estimate kinetic parameters for DOC removal. These regressions were computed using SigmaPlot 11.02

(SigmaPlot 2009). Solutions to the advective-dispersion equation used to illustrate the effects of DOC removal kinetics on DOC concentrations in groundwater were obtained using the method of Domenico (1987). The EPA Bioscreen software package (EPA 2016), which incorporates the analytic solution provided by Domenico (1987), was used to solve the advective-dispersion equation. Values for the longitudinal hydrodynamic dispersion tensor used in the advective-dispersion equation were estimated from a dispersivity (0.66 m) appropriate for the horizontal scale of the solution domain (200 m; Gelhar et al. 1992) and the simulated groundwater velocities.

## Results

### DOC concentrations and UV absorbance in groundwater

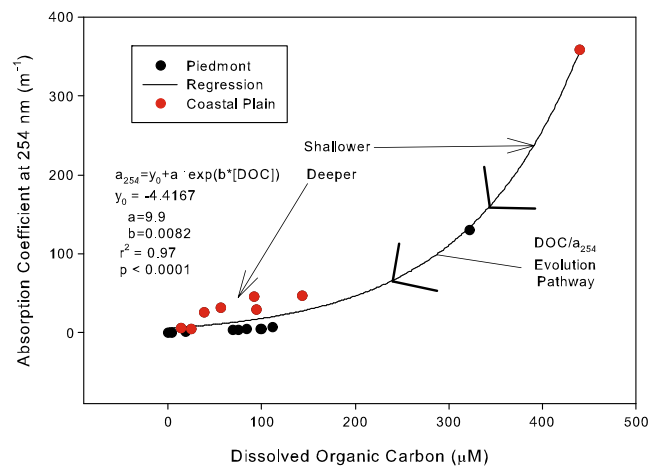
DOC concentrations in SC Piedmont groundwater show a strong inverse correlation to the thickness of the overlying unsaturated zone (Fig. 2a) indicating substantial DOM removal during transport. This reflects the fact that CDOM in soil and surface water must traverse an unsaturated zone comprised of clayey saprolite in order to reach the water table (Shen et al. 2015). Similarly, in a network of wells screened at multiple depths in a shallow Coastal Plain aquifer overlain by a uniformly thin unsaturated zone (~2 m) in South Carolina (the SC Coastal Plain site in Fig. 1; Chapelle et al. 2011), DOC concentrations also show a statistically significant inverse



**Fig. 2** **a** Dissolved organic carbon concentrations versus thickness of the unsaturated zone in the South Carolina Piedmont aquifer and **b** dissolved organic carbon concentrations versus well depth in the SC Coastal Plain aquifer

correlation to well depth (Fig. 2b). The wells tapping this surficial coastal plain aquifer are located in a recharge area and groundwater flow is predominantly downward; thus, well depth is a rough surrogate for the distance that groundwater has moved along aquifer flowpaths. Studies in other groundwater environments have also reported an inverse relationship between DOC concentrations and the thickness of the unsaturated zone (Pabich et al. 2001; Chapelle et al. 2013), and DOC concentration decreases along discrete groundwater flowpaths (Findlay and Sobczak 1996; Baker et al. 2000). The decrease in DOC concentrations has been attributed to a combination of biodegradation (Findlay and Sobczak 1996; Baker et al. 2000; Rauch and Drewes 2005; Grünheid et al. 2005), sorption onto aquifer materials (Neff and Asner 2001; Kalbitz et al. 2003), and dilution (Foulquier et al. 2010).

The observed decreases in DOC concentrations during transport in groundwater of the SC Piedmont and SC Coastal Plain aquifers are mirrored by decreases in UV absorption coefficients ( $a_{254}$ ; Fig. 3). This reflects the fact



**Fig. 3** Evolution of DOC concentrations and UV absorption coefficient ( $a_{254}$ ) along the flowpath for groundwater in South Carolina Coastal Plain (red) and Piedmont (black) aquifers

CDOM makes up a portion of DOC present in both ground- and surface waters and as DOC is removed,  $a_{254}$  decreases proportionally (Weishaar et al. 2003). The evolution pathway observed for DOC concentrations and  $a_{254}$  in the SC Piedmont and Coastal Plain aquifers (Fig. 3) is exponential and reflects the systematic removal of DOC, and associated CDOM, during transport through both the unsaturated and saturated zones. The slope of this evolution pathway reflects the sum of the operative DOC-removal processes. In addition, the exponentially decreasing shape may reflect the fractionation of DOM due to biodegradation and sorption. Previous studies (Meier et al. 1999; Guo and Chrover 2003) have shown that sorption of DOM to mineral surfaces can result in the removal of the more aromatic and hydrophobic molecules that contribute to CDOM. These processes were invoked in the “regional chromatographic model” proposed by Shen et al. (2015) to explain observed differences between the DOC composition of surface waters recharging the SC Piedmont aquifer, and the DOC composition of the underlying groundwater.

The observed patterns of DOC concentrations and  $a_{254}$  shown in Figs. 2 and 3, which occur over distances of tens of meters, imply that the kinetics of DOC removal are relatively rapid. However, lacking precise knowledge of soil water and groundwater seepage rates, and initial and final DOC concentrations (Findlay and Sobczak 1996; Baker et al. 2000; Rauch and Drewes 2005; Grünheid et al. 2005), the kinetics of DOC removal cannot be quantified using the data of Figs. 2 and 3.

### DOC concentration changes over time

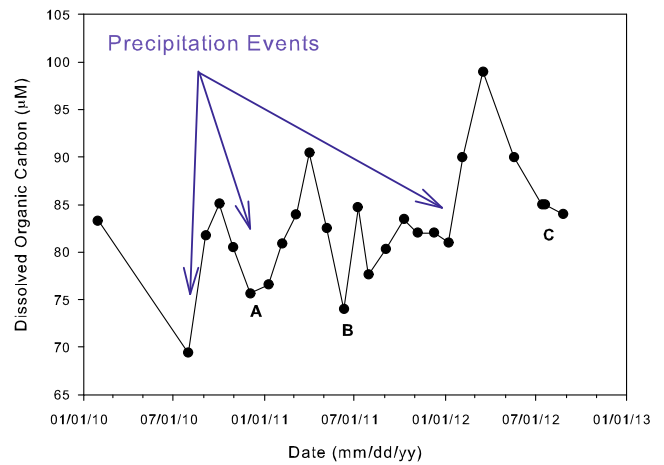
The changes in DOC concentrations and  $a_{254}$  in groundwater of the SC Piedmont and Coastal Plain aquifers (Figs. 2 and 3) represent samples collected at one discrete point in time. In

order to investigate variations in DOC concentrations over time, samples of groundwater from a USGS long-term monitoring well in the SC Piedmont aquifer were collected monthly for 2 years as described previously by Shen et al. (2015). During the 2-year period, concentrations of dissolved oxygen (DO) ranged from 0.6 to 1.2 mg L<sup>-1</sup>, temperature ranged from 15 to 16 °C, specific conductivity ranged from 899 to 976 μSi/cm, and concentrations of dissolved iron (0.03 mg L<sup>-1</sup>) and dissolved sulfide (<0.01) were consistently low. These data indicate that oxic conditions characterized by relatively low DO concentrations were predominant in groundwater tapped by the monitoring well.

DOC concentrations were observed to vary over time (between 100 and 70 μM; 1.3–0.91 mg L<sup>-1</sup>; Fig. 4), and the higher DOC concentrations correlated significantly to the amount of atmospheric precipitation recorded over 27 days prior to well sampling (Shen et al. 2015). Shen et al. (2015) interpreted these data as indicating that precipitation events (rainfall) mobilized DOM from the forest-floor leaf litter (Qualls and Haines 1992), and carried it to the water table resulting in a pulsed increase in groundwater DOC concentrations. Conversely, during periods lacking significant precipitation, DOC concentrations were observed to decline rapidly reflecting a combination of biodegradation and sorption of DOC onto aquifer material (Shen et al. 2015). The alternating trends of increasing and decreasing DOC concentrations over time due to pulsed precipitation events (Fig. 4) suggest that it may be possible to quantify DOC removal kinetics using these data.

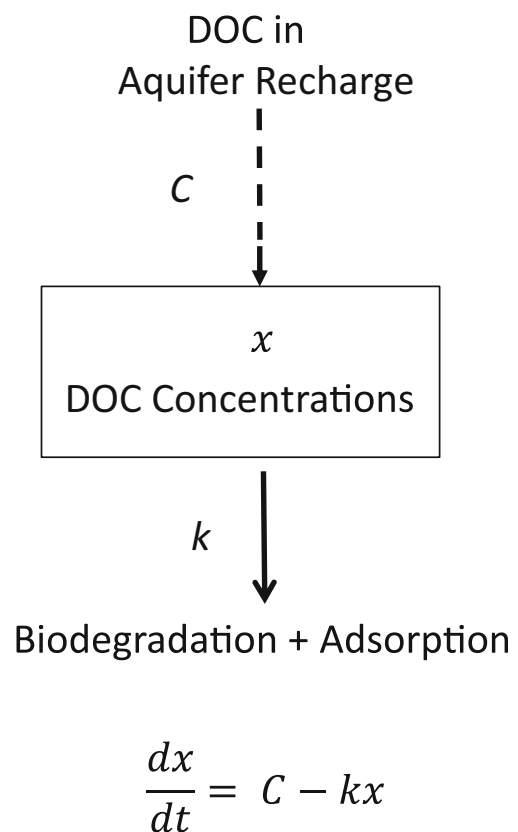
**Discussion**

In order to use the data of Fig. 4 to quantify DOC removal kinetics, it is first necessary to construct a model from which the kinetics can be quantified using the time-series data. Compartment models have been previously used to describe the transfer of DOM between different pools (surface liter, dissolved, adsorbed, etc) in order to calculate DOC fluxes through soils (Neff and Asner 2001). A simplified version of this compartment-model approach can be adapted to quantify the kinetics of DOC removal from groundwater. In this conceptualization (Fig. 5), aquifer recharge originating at land surface periodically delivers relatively high concentrations of DOM to the water table where it mixes and dilutes with ambient groundwater resulting in increased DOC concentrations. These increased DOC concentrations immediately become subject to biodegradation and sorption processes that begin to remove DOC from solution. The single-compartment model shown in Fig. 5 can be thought of as corresponding to the “soil soluble” compartment in the model of Neff and Asner (2001). DOC (denoted *C* in Fig. 5) enters the compartment (the fractured-rock aquifer) via surface-derived recharge



**Fig. 4** Dissolved organic carbon concentrations in a single well tapping South Carolina Piedmont rocks varying over a 2-year period, showing that increasing DOC concentration trends correspond to major precipitation events and decreasing DOC concentration trends correspond to the lack of major precipitation events (modified from Shen et al. 2015). Labels *A*, *B* and *C* relate to time periods (see Fig 6)

water, and the dashed line indicates that *C* is independent of the concentration of DOC already present in the compartment (denoted as *x* in Fig. 5). Surface-derived recharge then mixes



**Fig. 5** A one-compartment model showing dissolved organic carbon concentrations (*C*) delivered to groundwater by aquifer recharge and removed (*kx*) by biodegradation and adsorption processes. [*x*=concentration of *DOC* in the compartment (μM), *k* is a first order removal constant (T<sup>-1</sup>)]

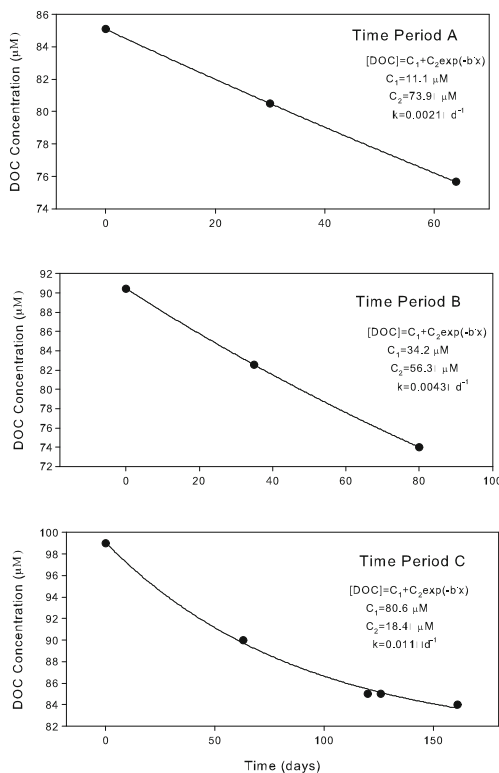
and dilutes with ambient groundwater (Foulquier et al. 2010) leading to an initial DOC concentration. DOC is then removed from the aquifer/compartiment by the combined effects of biodegradation and sorption. The removal rate ( $k$ ), which does not distinguish the relative contribution of biodegradation and sorption, is proportional to DOC concentrations in the compartment ( $x$ ). This leads to a differential equation describing DOC concentrations in the compartment as a function of time that is written:

$$\frac{dx}{dt} = C - kx \quad (2)$$

Where  $x$  = concentration of DOC in the compartment ( $\mu\text{M}$ ),  $C$  is DOC added by recharge ( $\mu\text{M}$ ), and  $k$  is a first order removal constant ( $\text{T}^{-1}$ ). By separation of variables, Eq. (2) has the solution:

$$x(t) = C_1 + C_2 e^{-kt} \quad (3)$$

Where  $x(t)$  are DOC concentrations as a function of time in micromoles per liter ( $\mu\text{M}$ ),  $C_1$  and  $C_2$  are constants of integration ( $\mu\text{M}$ ), and  $k$  is the first-order removal rate constant ( $\text{T}^{-1}$ ). When  $t=0$ ,  $x = C_1 + C_2$ , which is the initial concentration of DOC in the aquifer following a recharge event. As  $t$  becomes large following the recharge event, the second term of Eq. (2) approaches zero and  $x(t) \rightarrow C_1$ .  $C_1$ , therefore, represents DOC

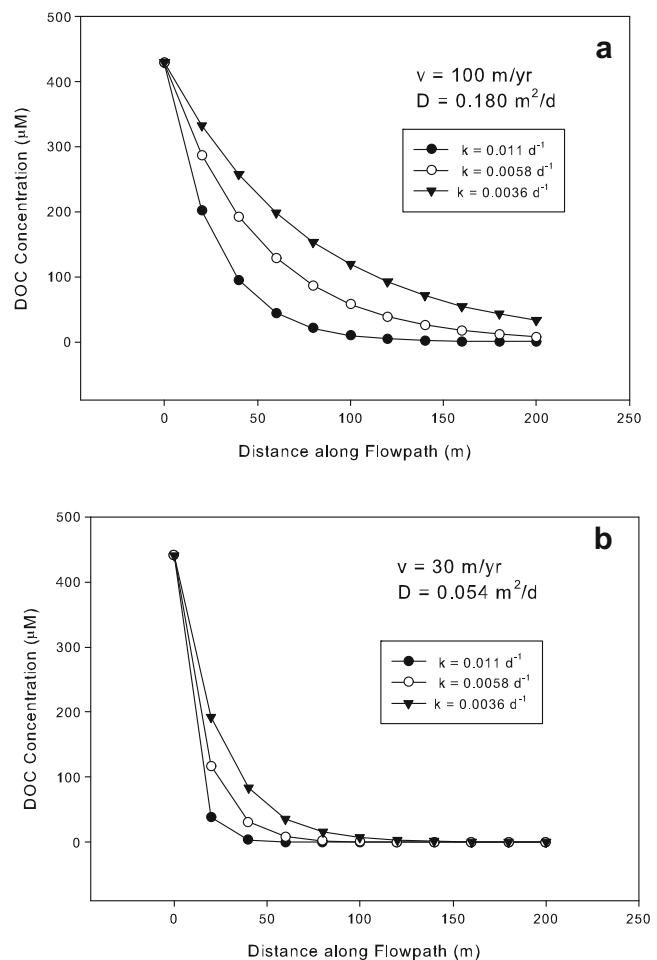


**Fig. 6** DOC concentrations versus time measured in the long-term monitoring well regressed to Eq. (2) for time periods A, B, and C (Fig. 4)

that is recalcitrant to biodegradation and sorption and thus remains in solution after the reactive DOC fraction ( $C_2$ ) has been removed (Grünheid et al. 2005).

The transient DOC data set includes three separate time periods where DOC concentrations declined for at least three successive sampling events, and these are labeled A, B, and C in Fig. 4. Because the compartment model includes three parameters ( $C_1$ ,  $C_2$ , and  $k$ ), a minimum of three data points are needed to yield parameter estimates. This precludes using instances in the data set where DOC concentrations declined over only one or two sampling events. This, in turn, may limit the accuracy of the parameter estimates for DOC removal. Regressing the data from time periods A, B, and C to Eq. (3) yields estimates of the parameters  $C_1$ ,  $C_2$ , and  $k$  as shown in Fig. 6. This, in turn, allows us to quantify the kinetics of DOC removal from groundwater due to the combined effects of biodegradation and sorption. To the authors' knowledge, this is the first time this compartment model approach has been used to quantify DOC removal kinetics in groundwater.

The estimates of DOC loss range from 0.093 to 0.21 micromoles per liter per day ( $\mu\text{M d}^{-1}$ ) and the DOC removal rate



**Fig. 7 a–b** Simulated transport of DOC in groundwater using the range of removal constants ( $k$ ) shown in Fig. 6

constants for time periods A, B, and C range from 0.0021 to 0.011 d<sup>-1</sup> (Fig. 6). Biodegradation experiments conducted with groundwater produced from the observation well by Shen et al. (2015) estimated a biodegradation rate constant of 0.0032 d<sup>-1</sup>, suggesting that biodegradation is the predominant process causing the observed DOC concentration declines over time. Regardless of the relative contribution of the different removal processes, these estimates indicate that the removal rate of DOC is relatively rapid, ranging from about 1.1 to 0.21 % d<sup>-1</sup>. The range of DOC removal rates and the rate constants associated with DOC removal estimated in this study are broadly consistent with rates observed in other groundwater systems (Findlay and Sobczak 1996; Baker et al. 2000; Rauch and Drewes 2005; Grünheid et al. 2005). This, in turn, suggests that the kinetics of DOC

removal are similarly rapid in a variety of groundwater systems.

The hydrologic significance of such rapid DOC removal rates can be illustrated by considering solutions to a one-dimensional groundwater advective-dispersion equation that incorporates the estimated removal kinetics (Domenico 1987):

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} - kC \tag{4}$$

Where  $C$  = concentration of DOC ( $\mu\text{M}$ ),  $t$  = time (T),  $D$  = longitudinal hydrodynamic dispersion coefficient tensor ( $\text{L}^2\text{T}^{-1}$ ),  $v$  = groundwater seepage velocity ( $\text{LT}^{-1}$ ), and  $k$  = first order removal rate constant incorporating both sorption and biodegradation of DOC from the dissolved phase ( $\text{T}^{-1}$ ).

**Fig. 8** DOC concentrations and UV absorbance for eight aquifer systems of the United States plotted against **a** the DOC/ $a_{254}$  evolution pathway exhibited by the SC piedmont and coastal plain aquifers for the entire concentration range shown in Fig. 3, and **b** for DOC concentrations between 0 and 100  $\mu\text{M}$

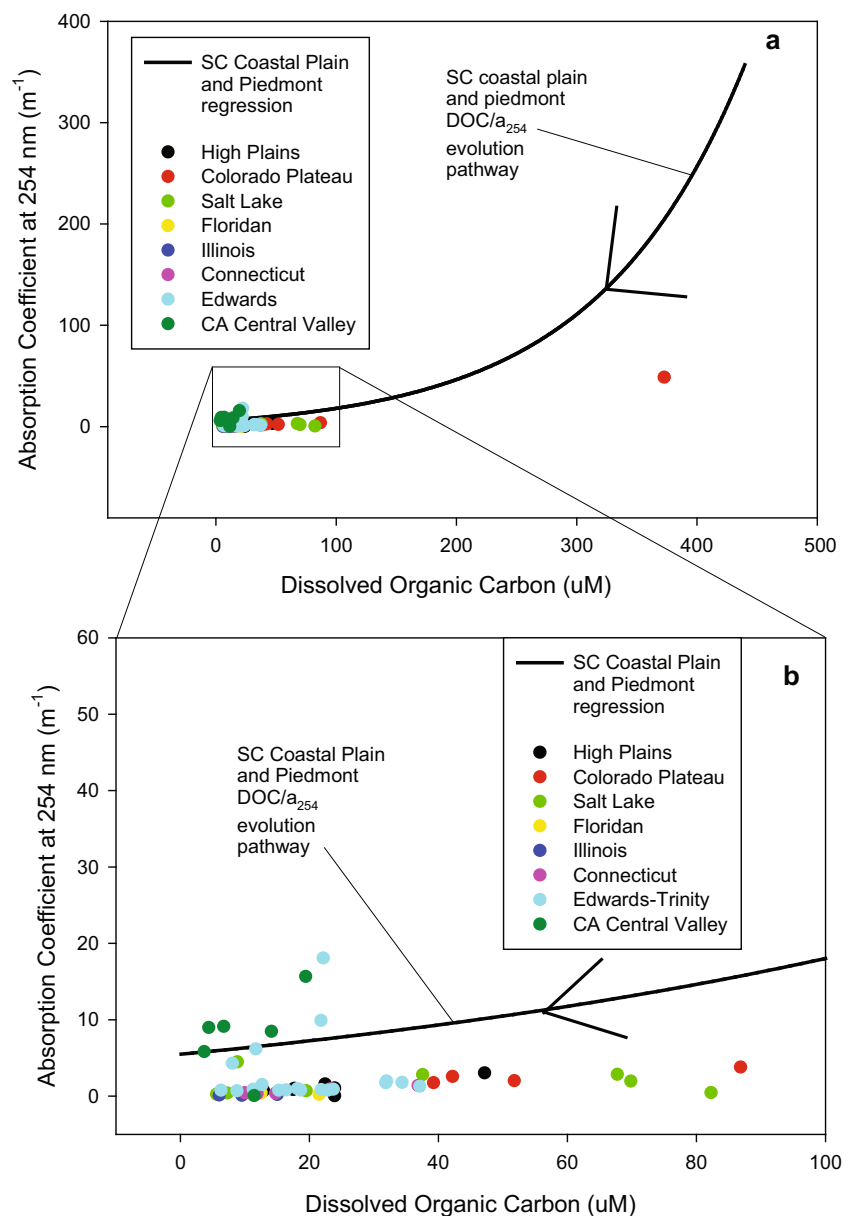


Figure 7 shows several example steady-state solutions to Eq. (4) for the three estimated DOC removal rate constants and for simulated groundwater seepage velocities of 100 and 30 m yr<sup>-1</sup>.

These simulations indicate substantial removal of DOC from groundwater in less than 200 m of flowpath and in less than 2 years of transport time. A groundwater seepage velocity of 100 m/yr<sup>-1</sup> is relatively high (Gelhar et al. 1992), but is representative of karstic carbonate aquifers such as the Floridan aquifer in southern Georgia (McConnell and Hacke 1993); thus, the 100 m yr<sup>-1</sup> simulation illustrates the higher end of both transport time and distance. As seepage velocity decreases, the distance and time of DOC transport decreases proportionally (Fig. 7b). The simulations of Fig. 7 show DOC concentrations approaching zero over time, which is equivalent to setting  $C_1$  in Eq. (3) equal to zero. In reality, it is observed that  $C_1$  is greater than zero in groundwater systems (Fig. 6), representing relatively non-reactive DOC, and DOC concentrations approach that value ( $C_1$ ) during transport (Grünheid et al. 2005).

The simulations shown in Fig. 7 are broadly consistent with empirical studies in a variety of groundwater systems which have reported substantial DOC removal over flowpath lengths of tens to hundreds of meters (Findlay and Sobczak 1996; Baker et al. 2000; Rauch and Drewes 2005; Grünheid et al. 2005). Finally, these simulations are consistent with the observed rapid loss of both DOC and color along the flowpath of the Floridan aquifer in response to recharge from the black-water Withlacoochee River in southern Georgia (McConnell and Hacke 1993).

### Similarity of DOC concentrations and UV absorbance in different groundwater systems

The rapid kinetics of DOC removal from groundwater (Fig. 7), and the similarity of these kinetics in different groundwater systems, suggests that the evolution pathways of DOC concentrations and  $a_{254}$  may be similar in different aquifers. Figure 8a shows DOC concentrations and  $a_{254}$  values in groundwater samples collected from 59 wells tapping eight different aquifer systems of the United States. These data cluster at the terminus of the DOC/ $a_{254}$  evolution pathway observed for the SC Piedmont and SC Coastal Plain aquifers as defined in Fig. 3. The sole exception to this clustering is a sample obtained from a deep hydrocarbon-producing zone of the Colorado Plateau aquifer. That, in turn, indicates that aquifers with large pools of fossil DOM sources can exhibit DOC and  $a_{254}$  values distinctly different from aquifers in which the principal source of DOM is surface-derived organic litter. In general, however, this clustering suggests that DOC/ $a_{254}$  evolution pathways exhibited by different aquifers may be similar.

A closer look at the DOC concentrations between zero and 100  $\mu\text{M}$  and the corresponding  $a_{254}$  values (Fig. 8b) reveals variability in the data that is not apparent at the scale of Fig. 8a. First, the majority of the DOC/ $a_{254}$  values fall below the SC Piedmont and Coastal Plain curve, although the slope of the curve is similar to the slope of the observed data. Secondly, several of the samples from the Edwards-Trinity aquifer and California Central Valley aquifer plot above the SC Piedmont and Coastal Plain curve. Those samples were characterized by relatively high nitrate concentrations ( $\sim 500 \mu\text{M}$ ). Because dissolved nitrate is a UV chromophore (Collos et al. 1999), this may contribute to the elevated  $a_{254}$  values relative to the lower-nitrate ( $< 80 \mu\text{M}$ ) groundwater produced from the other aquifers. This also illustrates that CDOM is not the only chromophore that can be found in groundwater. The rest of the observed variability may reflect (1) differences in DOM quality in the water recharging these different aquifers, (2) differences in aquifer material that exhibits different sorption behavior to DOM and (3) differences in redox conditions and available terminal electron acceptors that influence the bioavailability of DOM.

Groundwater ages for the aquifer systems sampled for this study have been evaluated with a variety of techniques including tritium, chlorofluorocarbons, and carbon-14 (DeSimone et al. 2014; Katz 2004; McMahan et al. 2004). Mean groundwater ages (time since recharge) for the eight aquifer systems range from a low of 10 years (Connecticut) to greater than 15,000 years (Colorado Plateau). Given the rapid rate of DOC removal suggested by the simulations of Fig. 7, groundwater from each of the eight aquifer systems will have undergone substantial DOM removal prior to the time of sampling. This, in turn, provides an explanation for the clustering of median DOC concentrations (17.6  $\mu\text{M}$ ; 0.22 mg L<sup>-1</sup>) and median  $a_{254}$  values (0.92 m<sup>-1</sup>) for the samples shown in Fig. 8.

These results are broadly consistent with those of Leenheer et al. (1974) in a survey of DOC concentrations measured in groundwater produced from 100 wells located throughout the United States which reported a median DOC concentration of 54  $\mu\text{M}$  (0.7 mg L<sup>-1</sup>). This suggests that background concentrations of relatively non-reactive DOC in groundwater ( $C_1$  in Eq. 3) are typically on the order of 20–75  $\mu\text{M}$  (0.26–1 mg L<sup>-1</sup>). Interestingly, the range of  $C_1$  values indicated by Fig. 8 is similar to the  $C_1$  estimates observed from the long-term monitoring well data (Fig. 6). Finally, and also consistent with the current results (Fig. 8), Leenheer et al. (1974) reported that DOC concentrations did not vary significantly between aquifers of different lithologies.

### Conclusions

The results of this study provide an explanation for the nearly uniform optical clarity that characterizes groundwater in a



variety of geologic media and under different hydrologic conditions. Whereas waters originating at land surface and recharging groundwater systems often contain high concentrations of CDOM, this CDOM is rapidly attenuated in the unsaturated zone overlying aquifers and in the saturated zone of the aquifers. Virtually any groundwater that has been recharged from land surface, and which has circulated in the subsurface for more than a few years, will have had much of its CDOM removed. This is why the springs tapping the Floridan aquifer, which are recharged by high CDOM surface waters, produce brilliantly clear water (Schmidt 2001) despite being relatively young (~20 years since recharge; Katz 2004). The striking clarity of these and other ground- and spring-waters, therefore, is a direct result of the rapid removal kinetics of DOM in groundwater systems.

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