

ABIOTIC NATURAL DISSOLVED ORGANIC MATTER-CARBONATE
INTERACTION IN KARSTIC AQUIFERS

By

JIN JIN

A THESIS PRESENTED TO THE GRADUATE SCHOOL
OF THE UNIVERSITY OF FLORIDA IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF
MASTER OF SCIENCE

UNIVERSITY OF FLORIDA

2009

© 2009 Jin Jin

To my family

ACKNOWLEDGEMENTS

I would like to sincerely thank my advisor, Dr. Andrew Zimmerman, for his continuous advice and guidance throughout my graduate study in the Department of Geological Sciences. His patience and encouragement helped me overcome lots of difficulties and eventually accomplish this research project. I am also very grateful to my committee members, Dr. Jonathan Martin and Dr. Jean-Claude Bonzongo, for all the help and support they provided during my experiments and thesis development. I thank all my friends in the Department of Geological Sciences for their friendship and laughter. Special thanks go to my lab mates, Atanu Mukherjee, Dr. Mi-Youn Ahn, Ann Laffey and Dr. Gabriel Kasozi, for their assistance in my research as well as the good time we shared together. Lastly, I would like to thank my beloved parents, who raise me up to more than I can be.

TABLE OF CONTENTS

	<u>Page</u>
ACKNOWLEDGEMENTS.....	4
LIST OF TABLES.....	7
LIST OF FIGURES.....	8
ABSTRACT.....	9
CHAPTER	
1 INTRODUCTION.....	11
2 BACKGROUND.....	14
NDOM in Groundwater.....	14
NDOM-Carbonate Interactions.....	17
3 MATERIALS AND METHODS.....	24
4 RESULTS.....	30
Quantity of NDOM-Carbonate Adsorption.....	30
Composition of NDOM-Carbonate Adsorption.....	32
5 DISCUSSION.....	45
Factors Controlling Karst Aquifer NDOM Adsorption.....	45
NDOM Transformation due to Abiotic Carbonate Interaction.....	52
NDOM Effect on Carbonate Dissolution.....	55
6 AQUIFER ENVIRONMENTAL IMPLICATION AND CONCLUSION.....	59
APPENDIX	
A DETAILS OF ANALYTICAL METHODS USED.....	62
B FLORIDAN AQUIFER GEOLOGIC FRAMEWORK.....	64
C ALTERNATIVE ADSORPTION MODEL PARAMETERS.....	65
D SORBENT X-RAY DIFFRACTION RESULTS.....	66
E HPLC PEAK RETENTION TIME OF SORBENT INDIGENOUS ORGANIC MATTER.....	68

F EEM GRAPHS FOR NDOM-SORBENT PAIRS	69
LIST OF REFERENCES	80
BIOGRAPHICAL SKETCH	91

LIST OF TABLES

<u>Table</u>	<u>Page</u>
3-1 Sorbent background information	29
3-2 Sorbent chemical composition.....	29
4-1 Linear model parameters (weight-normalized)	36
4-2 Linear model parameters (surface area-normalized)	36
4-3 Amount NDOM adsorbed at two NDOM solution concentrations	37
A-1 Calibration of the HPLC-SEC column	63
C-1 Langmuir model parameters (weight-normalized)	65
C-2 Freundlich model parameters (weight-normalized).....	65
E-1 HPLC peak retention time of sorbent indigenous organic matter	68
F-1 EEM graphs for NDOM-sorbent pairs	70

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
4-1 Adsorption data for soil NDOM on R-O and R-S carbonate rocks of two grain size fractions (<0.15 and 0.15-0.5 mm) and for 2 and 4 day interaction periods	38
4-2 Adsorption data for stream NDOM on six carbonate sorbents (C-S, C-H, C-A, C-O, R-O and R-S)	39
4-3 Adsorption and desorption data for soil NDOM on R-S of two grain sizes (<0.15 and 0.15-0.5 mm), 4-days	40
4-4 Representative EEM and change in EEM during interaction	41
4-5 Excitation-emission matrices of indigenous organic matter released from aquifer core materials (C-S, C-H, C-A and C-O, all <0.15 mm) into water	42
4-6 Liquid size exclusion chromatograph (HPLC-SEC) of soil NDOM (14.47 mg C/L) sorbate before and after interaction with four aquifer core materials	43
4-7 Ca ²⁺ and Mg ²⁺ released during 2-day interaction of distilled water and three concentrations of stream NDOM with aquifer core materials (C-S, C-H, C-A and C-O, all 0.15-0.5 mm)	44
5-1 Plot of sorbent surface area (m ² /g sorbent) versus adsorption affinity (L/g sorbent) for six Floridan Aquifer materials	57
5-2 Plot of sorbent indigenous organic matter content (g C/g sorbent) versus adsorption affinity (L/g sorbent) for six Floridan Aquifer materials	58
A-1 HPLC-SEC column calibration function	63
B-1 Floridan Aquifer geologic framework	64
D-1 Sorbent X-ray diffraction results	66

Abstract of Thesis Presented to the Graduate School
of the University of Florida in Partial Fulfillment of the
Requirements for the Degree of Master of Science

ABIOTIC NATURAL DISSOLVED ORGANIC MATTER-CARBONATE INTERACTION IN
KARSTIC AQUIFERS

By

Jin Jin

May 2009

Chair: Andrew R. Zimmerman
Major: Geology

Natural dissolved organic matter (NDOM)-mineral interaction (e.g. adsorption, desorption, mineral precipitation/dissolution) may be a significant factor controlling geochemical and microbial processes, and contaminant fate in karst groundwater systems. Despite its importance, the abiotic interactions of NDOM with subsurface carbonate remains poorly understood. Our study examines the abiotic NDOM-carbonate interactions that take place in a karst aquifer through laboratory adsorption-desorption experiments using NDOM from soils and stream water collected in north Florida and six representative carbonate sorbents from each of the four major formations making up the Floridan aquifer.

While significant adsorption was observed at higher NDOM concentrations, in the lower natural range of NDOM concentrations, most carbonate materials released indigenous organic matter (OM). No difference was found in the amount of organic carbon adsorbed from the two different NDOM types onto carbonate sorbents, however, the core materials generally sorbed more NDOM than aquifer rocks. Longer interaction periods for NDOM-carbonate led to more NDOM adsorption indicating that adsorption equilibrium was not achieved. Sorbent surface area was found to be a controlling factor of adsorption for relatively pure carbonate samples, but not

when sorbent indigenous OM and other impurities were present. The NDOM-carbonate adsorption system was well described by a modified linear isotherm, and was mostly reversible, though a small amount of hysteresis was observed.

Preferential adsorption of a high over low molecular weight NDOM, and a humic-like over fulvic-like fraction onto carbonate sorbents were detected. The presence of NDOM inhibited mineral dissolution, but the dissolution inhibition observed was not always proportional to NDOM solution concentration. Surface area, and more importantly, the mineralogy of carbonate sorbents were found to be the controlling factors in determining susceptibility to dissolution and degree of NDOM dissolution inhibition.

Though the NDOM-carbonate adsorption mechanism could not be completely determined by these experiments because of the heterogeneity and complexity of NDOM and adsorbent surfaces, it is clear that both rapid and weak outer-sphere bonding and stronger but slower hydrophobic interaction are at play. The results presented here provide a starting point for further studies examining subsurface NDOM-carbonate interaction, as well as some insight into the possible environmental consequences of human introduction of NDOM-rich solutions into aquifers that may occur during aquifer recharge or storage and recovery projects.

CHAPTER 1 INTRODUCTION

While groundwater aquifers hold 97% of the Earth's unfrozen fresh water (Hancock *et al.*, 2005), our understanding of the biogeochemical processes occurring there remains very limited. Although it has long been known that water and its solutes, microbes and rock interact in these subsurface systems, the importance and rates of the various biotic and abiotic geochemical reactions that occur there remain poorly defined. One example, the interaction of natural dissolved organic matter (NDOM) with solid surfaces in aquifers, has not received the scientific attention that it warrants, as it likely plays a major role in controlling groundwater quality.

Karstic aquifers, provide 40% of the groundwater used for drinking and more than 25% of the world's human population lives above karst. With their relatively high surface connectivity and groundwater flow rates, these aquifers are particularly vulnerable to contamination from above (Lau & Mink, 1987). While NDOM, itself, is considered a contaminant in drinking water (Bob & Walker, 2001), it may contain organic contaminant compounds and also plays a role in aquifer contaminant fate and transport as a 'carrier' of contaminants in the dissolved or colloidal state (Frimmel, 1998). Many contaminants that are deemed as virtually immobile in aqueous systems can interact with NDOM or colloidal NDOM, resulting in migration of hydrophobic chemicals far beyond predicted distances. In addition, groundwater NDOM plays important roles in controlling biogeochemical processes by acting as proton donors and acceptors and as pH buffers, and by participating in mineral precipitation and dissolution, and by affecting the transport and degradation of pollutants (Findlay *et al.*, 2003; Frimmel, 1998; Gu *et al.*, 1994; Schlautman & Morgan, 1994). For example, NDOM is a 'food' source, fueling microbial activity and thus, contaminant degradation, and consumes oxygen, thus controls the oxidation state of the subsurface (Lovley & Chapelle, 1995). Groundwater NDOM is

likely to encourage the growth of potentially harmful microbial populations (Boyes & Elliott, 2006; Fisher *et al.*, 2006). The presence of NDOM considerably influences the mobilization and fixation of heavy metals (e.g., Zn, Cu, Pb, Cd, Hg, Cr, Co, U, Pu) (Lee *et al.*, 2005; Petrovic *et al.*, 1999). Due to its reactive nature, a thorough understanding of the processes which govern groundwater NDOM quantity and quality deserves investigation.

Interactions between NDOM and carbonate minerals such as calcite and dolomite, the major constituent of a karstic aquifer, can affect the subsurface environment. Sorption of NDOM onto aquifer minerals changes the physicochemical properties of the solid to a large extent, including the complexation, dispersity and surface electrical property (Davis, 1982; Dunnivant *et al.*, 1992; Gu *et al.*, 1994; Jardine *et al.*, 1989). Enhanced carbonate dissolution is another environmental concern of NDOM-carbonate interaction in a karstic aquifer. Organic acids occurring in NDOM and the production of CO₂ via heterotrophic microbial activity can both enhance carbonate mineral dissolution, leading to geological hazards such as land surface subsidence (Wu, 2003). Understanding of subsurface NDOM-carbonate interaction is also important to assess the biogeochemical consequences of hydrogeologic projects such as aquifer storage and recovery (ASR), a process by which groundwater is recharged through wells to an aquifer and extracted for human use at some later time, and aquifer recharge (AR). Lastly, NDOM-carbonate interaction, which occurs during primary and secondary petroleum migration, could play an important role in the final composition of subsurface petroleum reserves (Mazzullo & Harris, 1992).

In spite of its relevance to environmental and human health, very few studies have specifically examined NDOM-carbonate dynamics in karst. Because these systems may be hydrogeological complex and ill-defined, our research employs laboratory examinations of

carbonate-NDOM interaction as a starting point toward this goal. A range of karst materials from the Floridan Aquifer and NDOM types were combined *in vitro* and relevant geochemical measurements made such that the important abiotic processes that transform NDOM in the subsurface could be identified. An additional future goal would be to use both abiotic and biotic signature of NDOM interaction in groundwater system, if identifiable, to trace the sources and travel paths of groundwater in the subsurface.

CHAPTER 2 BACKGROUND

NDOM in Groundwater

NDOM is a ubiquitous component of natural waters and is derived from microbial, plant and animal matter and the products of their decomposition in various environmental systems. As the major form in which terrestrial organic matter is made available to subsurface microbial systems and transferred to the freshwater aquatic and, ultimately, marine realms, much research on NDOM chemistry and reactivity was carried out.

Although approximately 25% of NDOM can be characterized as amino acids, nucleic acids, carbohydrates, hydrocarbons, fatty acids or phenolic compounds, the vast majority of NDOM remains uncharacterizable on a molecular level. It is of complex and heterogeneous nature with a wide range of molar masses and chemical structures that give it a multifunctional role in the natural environment (Frimmel, 1998). However, it is commonly operationally defined as humic substances, including fulvic, humic and hydrophilic acid fractions, based upon its solubility at various pH conditions.

There are three main sources of NDOM to groundwater: organic matter (OM) deposits (e.g., buried peat, kerogen or coal), soil and sediment, and other water bodies (i.e. OM infiltrating into the subsurface from rivers, lakes, wetlands or marine systems) (Aiken, 2002). NDOM derived from different source materials should have distinctive chemical characteristics associated with those source materials. For instance, NDOM derived from higher plants have relatively large amounts of aromatic-C and phenolic content, and low N content. Microbially or algal-derived NDOM, on the other hand, has greater N content, and low aromatic-C and phenolic content (Aiken, 2002). The relative contributions of these sources of groundwater NDOM vary

between aquifer to aquifer and would be quantifiable were it not for the microbial and abiotic processes can slowly alter the structure and chemical reactivity of the NDOM.

A major factor responsible for NDOM attenuation is biodegradation by indigenous soil and aquifer microorganisms. The respiration rate, which is an index of subsurface microbial activity, varies along the flow path as groundwater transitions from oxic to anoxic conditions (Murphy & Schramke, 1998). In many pristine aquifers, where microbial activity is limited by the availability of electron donors (usually NDOM), dissolved inorganic carbon (DIC) accumulates slowly along aquifer flow paths and available electron acceptors are consumed sequentially in the order dissolved oxygen > nitrate > Fe (III) > sulfate > CO₂ (Chapelle, 2000). Thus, biodegradation rates in the subsurface are not only controlled by the physiological capacity of the microbes, but also by subsurface nutrients available to the microbes (Simoni *et al.*, 2001).

The transformation of NDOM fractions occurs during its travel through the subsurface. For example, high molecular weight (M_w) components of NDOM was found preferentially adsorbed to surfaces, and have lower mobility than smaller M_w components during groundwater travel (Rauch & Drewes, 2005). Unretarded transport of the hydrophobic and macromolecular NDOM also found after adsorption indicating NDOM can exhibit considerable mobility in an aquifer and NDOM could alter the transport of contaminant in groundwater (McCarthy *et al.*, 1993).

Groundwater OM is one of the concerns during the implementation and evaluation of hydrogeologic projects such as soil-aquifer treatment (SAT) and ASR for treatment of both reclaimed water (Pavelic *et al.*, 2005) and wastewater (Cha *et al.*, 2004; Rauch & Drewes, 2004), which indirectly influences the trace elements status in an aquifer, such as As (Arthur, 2002; Price & Pichler, 2006). It was reported that approximately 20-25% of the organic carbon (OC)

injected into a carbonate aquifer was removed through aerobic respiration and denitrification (Vanderzalm *et al.*, 2006). During SAT, transphilic and hydrophilic OM can be preferentially removed during SAT, including non-aromatic OM such as large molecule polysaccharides and protein (Drewes *et al.*, 2006). Biological processes are found to be the main contributor for the removal of OM, which interestingly appears to be a limiting factor for biomass growth in the system (Rauch & Drewes, 2005). Changes in OM chemical properties and M_w distribution were also found in a artificial groundwater recharge in Finland (Lindroos *et al.*, 2002).

Microorganisms, including bacteria, fungi, algae and protozoa, serve as geochemical agents in the subsurface by controlling a series of reactions that influence the subsurface environment. Microbes are capable of affecting the fate of groundwater NDOM, for example, catalyzing the oxidation of OM (Lovley & Chapelle, 1995). In addition, they also influence the chemical composition of groundwater, such as accumulation of dissolved iron, methane and H_2S (Lovley & Chapelle, 1995). The hydraulic property of an aquifer can also be affected by microbial processes. The production of CO_2 and organic acids can lead to increased mineral solubility, developing secondary porosity thus increasing permeability in aquifer (Chapelle, 2000). On the other hand, microbes are found to cause active or passive mineral formation by precipitation and subsequent nucleation of crystal formation (Ehrlich, 1998). A decrease in hydraulic conductivity also indicates clogging of a limestone fracture by groundwater microbes (Ross *et al.*, 2001).

In addition to biodegradation and NDOM-mineral interaction (discussed in following section), other major processes that are considered to control NDOM attenuation in the subsurface are co-precipitation and dilution (Leenheer, 2002). NDOM co-precipitation (with groundwater cations such as Al^{3+} and Ca^{2+}) is likely to be controlled by pH and Eh changes in

the subsurface. Lastly, factors such as rainfall, snowmelt, recharge, and evapotranspiration can affect dilution and precipitation of NDOM in an aquifer indirectly.

NDOM-Carbonate Interactions

Although a variety of minerals may exist in carbonate aquifers, we shall assume a predominantly calcite composition (Randazzo & Jones, 1997) for the purposes of discussion here. There are many possible abiotic interactions between NDOM and calcite that can be examined including adsorption, desorption, dissolution and precipitation. These abiotic reactions may also, in turn, influence the microbially-mediated fate or transformation of NDOM.

Adsorption: Adsorption of NDOM onto aquifer carbonate is a process that occurs when groundwater NDOM molecules accumulate on mineral surface (sorbents), whereas desorption is a phenomenon whereby NDOM is released from carbonate mineral surfaces or matrices.

Adsorption of organic compounds onto inorganic solid surfaces can significantly alter the physicochemical properties of the underlying solid, whose behavior (e.g., electrophoretic mobility, colloidal stability, transport, and interaction with environmental contaminants) may be dominated by the adsorbed NDOM (Dunnivant *et al.*, 1992; Gu *et al.*, 1995; Gu *et al.*, 1994; Jardine *et al.*, 1989). For example, most solid surfaces in natural groundwater systems are negatively charged due to adsorbed NDOM (Gu *et al.*, 1994; Liang *et al.*, 1993; McCarthy *et al.*, 1993; McKnight *et al.*, 1992). The adsorbed NDOM coatings may also render hydrophilic surfaces hydrophobic and more capable of sorbing organic contaminants (McCarthy & Zachara, 1989; Murphy *et al.*, 1992; Murphy *et al.*, 1990). This is especially important to many waste disposal sites where organic ligands were found to compete with NDOM for adsorption onto sorbent surfaces. Besides sorption onto inorganic solids, organic compounds can bind with NDOM in the soil or groundwater environment, and thus have a considerable effect on the

dissipation of organic pollutants during soil and aquifer remediation (Amiri *et al.*, 2005; Chen *et al.*, 2005; Chen & Xing, 2005; Raber *et al.*, 1998).

The adsorption and desorption mechanisms of NDOM on carbonate minerals are not yet completely understood due to the heterogeneity and complexity of NDOM and adsorbent surfaces. The major mechanisms proposed by which NDOM may adsorb onto sorbent surfaces include: (i) anion exchange (electrostatic interaction), (ii) ligand exchange-surface complexation, (iii) hydrophobic interaction, (iv) entropic effects, (v) hydrogen bonding, and (vi) cation bridging (Sposito, 2004). However, there are few direct measurements with which these mechanisms can be distinguished. Ligand exchange between surface-coordinated hydroxyl and H₂O and organic compounds is most often invoked to explain mineral oxide-NDOM adsorption. Adsorption of a fulvic acid on goethite, for example, involves the complexation between COO⁻ of fulvic acid and -OH of the goethite and is usually accompanied by an increase of pH, indicating that NDOM replaces hydroxyls on iron oxide surfaces (Tipping, 1981). However, Davis (1982) reported very little change in pH with the adsorption of NDOM onto aluminum oxide and speculated that the stereo-chemical arrangement functional groups (e.g., -COOH, -OH) in NDOM may play a role in determining which NOM molecules are adsorbed and which are not. A physical adsorption mechanism driven by favorable entropy changes has also been suggested as the dominant interaction mechanism in NDOM-soil adsorption system. For instance, Gu *et al.* (1994) showed that larger and more hydrophobic NDOM fractions were preferentially adsorbed by iron oxide over smaller size hydrophilic NDOM fractions.

Due to their high surface area homogeneous mineral surface, metal oxides are widely used in adsorption investigations, particularly iron and aluminum oxides (Gu *et al.*, 1994; Johnson *et al.*, 2004; Saito *et al.*, 2004; Yoon *et al.*, 2005). Preferential adsorption of higher Mw,

more aromatic, and more hydrophobic fractions of OM was reported (Hur & Schlautman, 2003; Meier *et al.*, 2004; Meier *et al.*, 1999), and the cause for which was ascribed to presence of aromatic structures and acidic groups, as revealed by the close relationship between maximum sorption and total acidity and the content of carboxyl-C (Kaiser, 2003). Tombacz *et al.* (2004) reported that humic acids can be bound to the most reactive surface sites on surface via complexation reaction. Some researchers pointed that sorbents mineralogy dominates the relation between OM adsorption and surface area (Kaiser & Guggenberger, 2003), while others believe that the number (and probably the position) of acidic groups attached to aromatics is the primary control of adsorption (Kaiser, 2003).

Clay minerals are also commonly studied geosorbents (Baham & Sposito, 1994; Kahle *et al.*, 2003; Kahle *et al.*, 2004; Petrovic *et al.*, 1999). Similar preferential adsorption phenomenon as observed in OM-metal oxides systems was also found when use clay minerals as sorbents (Hur & Schlautman, 2003; Kaiser, 2003; Wang & Xing, 2005). The adsorption affinity, capacity and desorption hysteresis were found correlated with structural features of the humic substances during their interaction with Na-kaolin clay (Balcke *et al.*, 2002). The surface of clay mineral is likely to be modified during OM adsorption (Tombacz *et al.*, 2004; Wang & Xing, 2005).

Unlike metal oxide and clay minerals, adsorption of organic compounds onto calcite has not been extensively investigated, but a few studies have reported significant adsorption. One study (Lee *et al.*, 2005) reported adsorption of Suwannee River humic acid (SRHA) onto calcite to be rapid and mostly irreversible, with corresponding changes in electrostatic properties. The sorption of soil humic acids onto calcite was investigated for quite a long time (Carter & Mitterer, 1978; Muller *et al.*, 1986; Petrovic *et al.*, 1999) and even a computer model (de Leeuw, 2004) was employed to elucidate the adsorption mechanism between organic molecules and polymorph

calcite. Depletion in organic acidic compounds in NDOM following calcite adsorption was ascribed to be preferential adsorption of these compounds to calcite (Carter, 1978; Muller *et al.*, 1986). Another study of the adsorption of benzoate, citrate, tartrate and glutamate on calcite concluded that adsorption of organic compound with carboxylic groups resulted in a negative surface charge imparted to calcite (Plank & Bassioni, 2007). However, all these previous used finely ground pure and highly crystalline carbonate minerals such as calcite and dolomite do not necessarily represent the adsorption behavior of NDOM that will be observed in karst aquifer.

Heterogeneous geosorbents such as aquifer rock, like soil and sediments, are complicated mixture of minerals that are expected to have a range of surficial properties and, therefore, behaviors with respect to NDOM adsorption. This is evident in the previous studies on OM adsorption to aquifer materials which have mainly been carried out in sedimentary, mainly sandy, aquifers. For example, it is reported that the behavior of NDOM sorption onto a sand and gravel aquifer is dominated by solid size fractions, as well as the ferrous minerals, which comprise only a small part of the aquifer material (Barber *et al.*, 1992). Studies examining the adsorption of phenols onto a sandy aquifer material revealed that sorption decreases with increasing DOC concentration and pH in the solution (Amiri *et al.*, 2005; Amiri *et al.*, 2004; Ball & Roberts, 1991a). An intraparticle diffusion model was utilized to explain the adsorption of halogenated organic chemicals to aquifer materials (Ball & Roberts, 1991b). The origin and long-term transport of high and low M_w DOC fractions were investigated in a clay-rich till aquitard system (Hendry & Wassenaar, 2005). Retardation of NOM in a field-scale test (in a sandy aquifer) proved the NOM adsorption phenomena that observed in laboratory studies (McCarthy *et al.*, 1993).

Adsorption mechanism has also been investigated on aquifer materials. For example, ligand exchange was regarded as the dominant reaction in sorption of fulvic and humic acids onto both synthetic (iron-oxide-coated quartz) and natural aquifer materials (soil and sediments) (Chi & Amy, 2004). In contrast, preferential adsorption of hydrophobic versus hydrophilic OM was also observed (Ussiri & Johnson, 2004), indicating the importance of hydrophobic interaction. Others have emphasized the importance of mineral texture on sorption processes. For example, a pore-filling mechanism was suggested by a study on low-polarity organic compounds (such as PAHs) sorption within a microporous aquitard (Xia & Ball, 1999). Similarly, entrapment of hydrophobic organic compounds in an aquifer kerogen isolate was explained by hole-filling mechanism (Ran *et al.*, 2004). A conceptual model was proposed to describe micro-scale, intergranular variability in sorption properties of the aquifer sediments (Barber *et al.*, 1992). However, no studies have examined the adsorption of bulk or NDOM fractions on natural heterogeneous carbonate materials.

Desorption: Desorption of NDOM in an aquifer system, whether partial or complete, can significantly affect the OM and aquifer solid, and thus controls the fate and transport of subsurface OM and other organic or inorganic contaminants. For example, slow desorption kinetics limits the efficiency of soil and groundwater remediation as well as the bioavailability of contaminants (Carmichael *et al.*, 1997; Karapanagioti *et al.*, 2001). When adsorption is irreversible, that is, the whole of the adsorbed NDOM cannot be completely desorbed under similar conditions, the system is termed ‘hysteretic’ (Dituro & Horzempa, 1982; Vaccari & Kaouris, 1988). Hysteresis was observed for a number of organic compounds adsorbed on soil sediments, pure clay minerals, and metal oxides (Barriuso *et al.*, 1992; Dituro & Horzempa, 1982; Pu & Cutright, 2006; Vaccari & Kaouris, 1988). However, strictly speaking, completely

irreversible reactions are thermodynamically impossible. Thus, the hysteresis of an adsorption-desorption reaction is often considered as an experimental artifact due to either kinetic limitation or other factors such as chemical and biological activities (Gu *et al.*, 1994). In any case, the degree to which adsorption of organic compounds may be reversible can be taken as an indication of the strength of the sorbent-sorptive interaction (Essington, 2004c).

Dissolution/precipitation: A unique feature of karst, versus other types of aquifers, is that dissolution/precipitations may occur on short (experimentally observable) timescales. An issue that is still debated is whether organic compounds enhance or inhibit the dissolution of carbonate minerals. Some organic compounds were shown to enhance dissolution (Fredd & Fogler, 1998; McMahon *et al.*, 1995; Perry *et al.*, 2003; Wu & Grant, 2002) or at least inhibit precipitation (Inskeep & Bloom, 1986; Lin & Singer, 2005; Lin *et al.*, 2004; Luttge & Conrad, 2004). Natural organic moieties such as acids may enhance calcite dissolution by simply releasing proton to the aqueous system (Equation 2-1):



Organic moieties may also fuel microbial respiration, producing CO_2 , which leads to calcite dissolution, following the overall reaction (Equation 2-2):



The calcite dissolution rate has also been found to increase significantly in the presence of chelating agents which bind calcium. A surface chelation mechanism was introduced to describe the dissolution and the rate of dissolution is found enhanced by the influence of proton attack at low pH (Fredd & Fogler, 1998; McMahon *et al.*, 1995; Perry *et al.*, 2003; Wu & Grant, 2002).

On the other hand, some compounds were shown to inhibit calcite dissolution as well as enhance precipitation (Frye & Thomas, 1993; Hoch *et al.*, 2000). The finding that compounds of

greater M_w and hydrophobicity (e.g., humic versus fulvic acids) inhibit calcite growth most (Hoch *et al.*, 2000; Lin & Singer, 2005; Lin *et al.*, 2004), indicates that surface coverage plays an important role. Thermodynamic modeling suggest that carboxylic acids, hydroxyl aldehydes, and amides will be effective crystal growth inhibitors through their strong adsorption to the growth steps, thereby blocking these sites to further attachment by calcium (de Leeuw, 2004).

Again, most previous research on the influence of OM on carbonate mineral dissolution or precipitation was carried out using pure mineral samples. Our study investigates the abiotic NDOM-carbonate rock interactions that may be predicted to take place in the Floridan aquifer through laboratory adsorption-desorption experiments using NDOM (collected from North Florida creeks and soil extracts) and aquifer materials. The present study is designed to be a starting point toward an understanding the range and complexity of behaviors of karst OM-carbonate subsurface system.

CHAPTER 3 MATERIALS AND METHODS

Since the main purpose of our study is to model and investigate subsurface abiotic NDOM-carbonate interaction, experimental conditions and materials were chosen to as to mimic, as closely as possible, the subsurface aquifer environment. Natural forest soil and stream water NDOM sources were used as the sorbate and various aquifer rocks and core material from a range of depths were used as sorbent. Two sorbent size fractions, and NDOM concentrations spanning the natural NDOM concentration range, were tested in batch adsorption experiments and chemical analyses of the solute composition before and after mineral interaction were used to understand the role of abiotic processes on NDOM transformation.

Sorbents: Adsorption experiments were carried out using two groups of aquifer materials: core material provided by the Florida Geological Survey (FGS) from regions of south-central Florida where ASR projects are underway, and relatively pure Floridan Aquifer rock, quarried and provided by the Florida Department of Transportation (FDOT) (designated C and R, respectively: Table 3-1). The original (before granulating) FDOT aquifer rocks are dense and relatively light-color carbonate comparing to FGS core material which were friable and brownish in color. The samples include representatives from each of these four major formations of the Upper Floridan Aquifer formations; Hawthorn, Suwannee, Ocala, and Avon Park (designated H, S, O and A, respectively: see Appendix II for Florida hydrogeologic framework). The major elemental composition of each FGS sample is shown in Table 3-2, as is the Brunauer-Emmett-Teller (BET) surface area determined by N₂ adsorption using a Quantachrome A1 Autosorb (Quantachrome Corp., Boynton Beach, FL). FGS core sorbent mineralogy was identified (by Dr. W. Harris, UF Soil and Water Science Department) using X-ray diffraction (XRD: see Appendix IV for figures). The C-A sample is nearly pure dolomite, C-O is nearly pure calcite, C-S is

mainly calcite and quartz, and the C-H sample has calcite, dolomite, quartz, apatite, and palygorskite. All samples were granulated and then sieved into <0.15 mm and 0.15-0.5 mm size fractions prior to surface area, XRD analysis, and adsorption experiments. The OM content of both FGS and FDOT samples was measured by loss-on-ignition (LOI, 450°C for 4.5 hours) and converted to organic carbon (OC) content assuming 0.5 g OC/g OM (Drever, 2002a; Essington, 2004a). Only C-H had a surface area and OC content significantly greater than the others, while the OC content of both rock samples were clearly lower than that of the core samples.

Sorbates: We have measured local groundwater samples ranging 0.5-13 mg OC/L and surface water concentrations ranging 1-32 mg OC/L, though OC concentrations in swamp waters can be significantly greater. The NDOM in most groundwater, however, is likely to be soil-derived (Tipping *et al.*, 1997). In our study, we use a north Florida mixed forest soil extract and stream water collected from Santa Fe River watershed, FL as the primary NDOM sources for adsorption experiments. For comparison, two other types of NDOM (two lakes near Gainesville, FL) were also tested as NDOM sorbates. Soil samples were 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, photo-oxidized OC-free water) to prepare sorbate NDOM solutions of various concentrations. The stream and lake NDOM samples were filtered, concentrated, stored and diluted in the same manner as the soil NDOM sample.

Adsorption and desorption experiments: Samples for batch adsorption experiments were prepared by mixing 40 ml background NDOM solutions (concentration ranges from 0 to

153.49 mg C/L) with amount of granulated aquifer materials that have 20 m² surface area in 50 ml polypropylene centrifuge tubes. Tubes were then placed 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 glass vials and stored in 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 of the adsorption experiment, tubes were weighed so that entrained solution amount could be calculated, and 40 ml OC-free water was added to each tube. Dissolved organic carbon (DOC) was then measured in the supernatant after another 4-day incubation period to determine the amount of OM desorbed.

The amount of DOC adsorbed onto or desorbed from carbonate surfaces was assumed to be the difference between DOC in starting and ending solution. Adsorption and desorption isotherms were constructed by plotting amount DOC adsorbed or desorbed (q_e , mg C/g sorbent) versus final equilibrium concentration (C_e , mg C/L) for a range of solution concentrations. The adsorption data were fit using three empirical adsorption models (linear, Freundlich and Langmuir). Model fits were quantified using least squares techniques. Although these three models can fit the data equally well (i.e. high R^2 values for each model, complete fitting parameters listed in Appendix III), as the simplest model with the fewest assumptions, the linear model was chosen as best in keeping with the principle of parsimony. In addition, a simple model is more easily applied to estimations of NDOM-carbonate adsorption in natural hydrogeologic system where, in many instances, the amount of data available is insufficient to

justify a more sophisticated approach. Lastly, many more complex adsorption models, including Freundlich and Langmuir, may reduce to linear model under certain restrictive assumption or at lower sorptive concentration ranges. The equation for linear isotherm is given as follows (Equation 3-1):

$$q_e = k_D C_e \quad (3-1)$$

where q_e is the amount of adsorbed sorptive, normalized to sorbent weight (in mg C/g sorbent), and C_e is the equilibrium organic carbon concentration in the background solution (in mg C/L). The distribution coefficient, k_D (in L/g sorbent), is a function of the properties of the sorbent and sorptive interaction and is often referred as an indication of adsorption affinity (Drever, 2002b; Essington, 2004d; Schwarzenbach *et al.*, 2003a). A slightly modified linear equation, which includes a y-axis intercept term, was employed in our study (Equation 3-2):

$$q_e = k_D C_e + b \quad (3-2)$$

This was done to express the amount of indigenous OM released from the aquifer materials.

Analytical Methods: Dissolved organic carbon was measured on a Shimadzu total organic carbon analyzer (TOC-5000A) after acidifying to pH 1 to 2 with 1M HCl and sparging for 2 minutes with OC-free air to remove inorganic carbon from samples prior to the measurement. The mean of three to five injections of 60 μ l is reported for every sample and precision, the coefficient of variance, was <5% for the replicate injections.

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 fluorescence spectrometer to obtain three dimensional excitation-emission matrix (EEM) spectra of the samples. This instrument is equipped with a xenon lamp that energizes the sample with nearly

constant intensity in the range from 200 to 800 nm. Excitation wavelengths from 200 to 450 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 700 nm at 3 nm intervals.

The molecular weight (M_w) distribution of NDOM before and after adsorption was determined by high performance liquid chromatography-size exclusion chromatography (HPLC-SEC) according to the methods of Chin (1994), modified by Zhou (2000). The liquid chromatography 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), purchased from Tosoh Bioscience LLC (Montgomeryville, PA) and compound detection was by UV-absorbance at 254 nm. A phosphate buffer was used as a mobile phase (0.1M NaCl, 0.002 M KH₂PO₄, and 0.002 M K₂HPO₄ buffered to pH 6.8) and flow rate was 1 ml/min. The HPLC-SEC was calibrated using four protein standards (albumin bovine, M_w =67 kD, ovalbumin M_w =45 kD, chymotrypsinogen A M_w =24 kD, and bacitracin M_w =1450 D; all purchased from MP Biomedicals) at concentrations of 110-260 ppm. Retention time was converted to molecular weight using the calibration curve (see Appendix I).

Major cations (Ca²⁺ and Mg²⁺) concentration and pH of the background solution, both before and after adsorption, were measured in order to detect possible mineral dissolution/precipitation reactions. Supernatant solutions were acidified to pH=1~1.5 and stored at 4°C before analysis using an automated Dionex DX500 ion chromatograph (Dionex Corp., Sunnyvale, CA). Internal standards reflect a precision of better than 3% of the value of the measurement.

Table 3-1. Sorbent background information

	Sample code used	Geologic formation	Location	Sample information/core depth
Core samples ^a	C-H	Hawthorn	Palm Beach County, FL	W-18728; 797-798 ft
	C-S	Suwannee	Collier County, FL	W-17801; 974-975 ft
	C-O	Ocala	Hendry County, FL	W-18720; 1190-1191 ft
	C-A	Avon Park	Osceola County, FL	W-18725; 980-985 ft
Rock samples ^b	R-S	Suwannee	Brooksville, FL	quarried
	R-O	Ocala	Newberry, FL	quarried

a. Core samples provided by the Florida Geological Survey (FGS), Tallahassee, FL.

b. Floridan Aquifer rock samples provided by Florida Department of Transportation (FDOT), Tallahassee, FL.

Table 3-2. Sorbents chemical composition

Sorbent	Sorbent surface area (m ² /g) ^a		Organic carbon content ^b	Major elemental composition (weight %) ^c								
	<0.15 mm size fraction	0.15-0.5 mm size fraction		SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅
C-H	9.6	13	1.29	17.7	1.9	0.3	3.2	38.9	0.7	0.5	0.1	6.4
C-S	3.9	4.1	0.38	15.3	0.6	0.1	0.5	45.6	0.2	0.2	bdl	0.3
C-O	0.7	1.7	0.74	0.5	0.2	bdl ^d	0.9	53.1	0.1	0.1	bdl	bdl
C-A	0.6	0.5	0.66	0.7	0.2	0.1	18.5	32.8	0.1	0.1	bdl	bdl
R-S	3.7	2.8	0.02	Not determined								
R-O	1.5	0.8	0.11									

a. Sorbents surface area (m²/g sorbent) determined using multipoint N₂ adsorption and calculated using BET theory.

b. Sorbent organic carbon content (in weight %) determined by loss-on-ignition (LOI) method (assuming organic matter composition of 50% organic carbon).

c. Major elemental composition data (in weight %) of sorbents provided by Florida Geological Survey, Tallahassee.

d. below detection limits

CHAPTER 4 RESULTS

Quantity of NDOM-Carbonate Adsorption

Four different types of NDOM (soil, stream and two lake NDOM) were tested using the same experimental treatment, but only soil and stream NDOM were selected for further investigation since the other two NDOM have similar chemical composition (i.e., EEM and HPLC results) as stream NDOM. Significant adsorption of both soil and stream-derived NDOM samples onto all carbonate rock sorbents was measured. Generally, there was no difference in the amount of DOC adsorbed from the two different NDOM samples onto carbonate sorbents, as all the adsorption data were within the confidence level of our isotherms. However, the FGS core materials generally sorbed more NDOM than FDOT aquifer rocks at the same background NDOM concentrations, indicating a greater adsorption affinity for the core materials. The FGS core materials showed release of indigenous rock OM when the concentration of background solution is low (especially in controls when background solution is OC-free DI water), while there was no such release for the FDOT aquifer materials. There was no significant pH change over the course of the 4-day adsorption period. Furthermore, the fine particle size fraction (<0.15 mm) for both aquifer rocks and core materials, although not very significant, tended to adsorb more NDOM than the coarse particle size fraction (0.15-0.5 mm).

Adsorption isotherms for soil NDOM on granulated aquifer rocks 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). This linearity extends to an equilibrium concentration of at least 153 mg C/L (Figure 4-1, model parameters in Table 4-1). In all cases, Suwannee formation rock (R-S), exhibited greater adsorption affinity (higher k_D) than Ocala formation rock (R-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 counterpart when expressed on a weight-normalized basis. There was no significant difference in k_D values, however, when surface-area normalized isotherms were plotted (Table 4-2).

Longer equilibration periods for NDOM-carbonate interaction (i.e. 4 versus 2 days) led to greater k_D values, though individual data points for 2 versus 4 day adsorption were not always significantly different. Therefore, our soil NDOM-carbonate adsorption system did not, technically, reach equilibrium in two or likely even four days and the full adsorption capacities of the sorbents remain unknown. Longer time period adsorption experiments were not carried out, however, due to the occurrence of dissolution (discussed later in text).

Two-day adsorption isotherms for stream NDOM (0-20 mg C/L) sorbed on each of the aquifer sorbents (C-S, C-H, C-A, C-O, R-O and R-S, all of 0.15-0.5 mm grain sizes) are plotted in Figure 4-2 (isotherm parameters in Table 4-1). In general, the isotherm linearity for FDOT aquifer rocks (average $R^2=0.9954$) is better than that of FGS core material (average $R^2=0.9701$, excluding C-A which has $R^2=0.4322$). The unexpectedly low R^2 for C-A (poor isotherm linearity), it is not likely caused by experimental error since experimental duplicate treatments are in close agreement (further discussion later in text). It is also clear from both plotted isotherms (Figure 4-2) and isotherm parameters (Table 4-1), that, unlike the aquifer rock isotherms with y-intercepts close to zero, those of aquifer core materials have negative values, implying that indigenous OM is released into solution. The amount of OM released from the C-O sample is greatest of all the aquifer sorbents tested, and sorption of NDOM only occurs at background solution concentrations greater than 13 mg C/L (Figure 4-2).

To make comparisons easier, the percent of NDOM adsorbed by sorbent at two background concentrations for each NDOM-carbonate pair was calculated using the linear

adsorption isotherms constructed (Table 4-3). At low NDOM concentration (i.e. 5 mg C/L), the adsorption percentage is relatively low, some of the treatments even show desorption (negative value). The adsorption percentage increases with the increasing of NDOM concentration. At a relatively high concentration (i.e. 20 mg C/L), the percentage for most the treatments fall in 30-70% range and 72.3% was observed as the highest, indicating there were still some ‘free’ NDOM in the solution that are ready to be adsorbed, and sorbents had been adsorbing maximum amount of NDOM in the given experimental time (2 or 4 days). Therefore, our adsorption systems were not restricted by the lack of enough NDOM in background solution, and our experimental design is fairly grounded.

Immediately after the 4-day adsorption, a 4-day desorption experiment for Suwannee and Ocala rocks was also carried out using OC-free DI water to replace the NDOM solution. Since both rocks have similar adsorption-desorption patterns, only Suwannee (both <0.15 mm and 0.15-0.5 mm) is shown (Figure 4-3). At the low solution concentrations at which desorption was carried out, only a small portion of the NDOM remained sorbed to the aquifer rocks. That is, a small amount of hysteresis is observed, indicating that adsorption was not perfectly reversible.

Composition of NDOM-Carbonate Adsorption

Chemical analyses of soil and stream NDOM (sorbates) both before and after mineral interaction were carried out to investigate the possibility of preferential adsorption of specific NDOM components.

Fluorometry: Fluorescence spectrometer is useful as a tool to compare the bulk fluorophore composition of heterogeneous samples such as NDOM. A representative EEM plot of soil NDOM (Figure 4-4) shows four main fluorophores types detected and their corresponding location in EEM space which were identified in the literature previously. They

include a fulvic-like peak (C: Excitation/Emission wavelengths 295-305 nm/410-420 nm), a humic-like peak (A: 210–260/410–450 nm), and two tryptophan-like peaks (T1: 275–280/340–360 nm and T2: 215–220/310–340 nm) (Coble, 1996). EEM graphs of stream NDOM are similar to that of soil extract but lack the tryptophan-like fluorophores (Peaks T1 and T2), which are believed to be related to microbial activity (Parlanti *et al.*, 2000). In addition, EEM identified the indigenous OM released from each of the core materials (into deionized OC-free water) as spectrophotometrically similar to each other as well as to stream water NDOM (Figure 4-5). That is, they lacked the tryptophan like fluorophores present in soil NDOM extract.

While EEM data for each NDOM-sorbent pair are presented in Appendix VI, a single representative EEM is shown here (Figure 4-4). The difference EEM (fluorescent intensity matrix of NDOM before carbonate rock interaction, on top, minus, background solution intensity EEM after interaction, on bottom), shows the fluorophores that preferentially adsorbed as negative value intensities. Humic-like fluorophores were found preferentially adsorbed over the other three fluorophores by core materials during two days interaction period as it exhibits negative peak on the difference EEM graph (Figure 4-4).

HPLC-SEC: Both NDOM sorbate types tested in our study displayed same Gaussian molecular weight distributions and retention times in size exclusion chromatograms. The average peak retention time of 11.7 ± 0.1 minutes (Figure 4-6), corresponds to a M_w of 30.6 ± 1.1 kD (calculated using the retention time- M_w linear relationship of protein standards, see Appendix I). Groundwater well sample collected from Santa Fe River Basin in north Florida were also found to have similar M_w distributions. These findings justify the use of soil and stream NDOM interchangeable and as representative of groundwater NDOM in the region.

Further, because freeze dried and non-freeze dried NDOM displayed the same M_w distribution, indicating little chemical change occurred during laboratory processing.

Two peaks were found in the chromatograms of indigenous OM via aquifer rock-DI water blank controls, with retention time of 11.9 (corresponding to 28.5 kD in M_w) and 12.7 minutes (19.7 kD), respectively. In addition to these two peaks, two other peaks were found in solution of core material-DI water controls: 5.9 (94.1 kD) and 16.2 minutes (~ 1000 D), indicating the difference in M_w distribution among indigenous OM of different sorbents and NDOM used as sorbate (Appendix V).

M_w distributions of both NDOM types decreased (longer peak retention time) following sorbent interaction (FGS core materials, 2-day interaction: example in Figure 4-6). Thus, there was preferential adsorption of larger M_w over smaller M_w compounds which was slightly less for C-A and C-O (a 1 minute retention time increase corresponding to about 10.9 kD), and slightly larger for C-S and C-H (a 2 minutes retention time increase, corresponding to about 21.9 kD). No HPLC evidence shows that the sorbent size has any effect on NDOM adsorption character.

Ion Chromatography: The concentrations of Ca^{2+} and Mg^{2+} ions in supernatant solutions following NDOM-carbonate interaction were measured to gauge the influence of NDOM on mineral dissolution after 2-day incubations of stream NDOM with FGS core material.

In experimental controls (DI water-sorbent pairs), mineral dissolution occurred (as gauged by Ca^{2+} release) that was greatest for C-H and least for C-A samples on a weight-normalized basis. On a surface area-normalized basis, however, these trends were just the opposite (Figure 4-7). In addition, samples of fine particle size (< 0.15 mm) released more cations to solution than those of the larger particle size fraction (0.15-0.5 mm).

Mineral dissolution was also detected after interaction with NDOM; however, the amount of cations released was decreased relative to that in DI water alone (Figure 4-7). Further, the decrease in mineral dissolution was enhanced with increasing concentrations of NDOM sorbent. This was observed for sorbents in both size fractions (<0.15 mm and 0.15-0.5 mm) and for both soil and stream NDOM. For example, after core materials (0.15-0.5 mm) two-day interaction with stream NDOM (concentration up to 18.19 mg C/L), on a weight-normalized basis, strongest Mg^{2+} dissolution inhibition was found in C-O (82.3% inhibition), followed by C-S (73.1%), while C-H and C-A experienced similar relatively lower inhibition (38.7% and 44.5%, respectively). The extent of Ca^{2+} dissolution inhibition does not synchronize with that of Mg^{2+} , with strongest inhibition found in C-A (66.6%) and weakest in C-H (16.2%). The same dissolution inhibition effect of NDOM also was found on a surface area-normalized basis (Figure 4-7).

Table 4-1. Linear model parameters (weight-normalized)

Experimental treatment ^a	k_D ^b	b ^c	R^2
R-S, <0.15 mm, soil NDOM, 4-day, adsorption	0.005	-0.011	0.997
R-S, <0.15 mm, soil NDOM, 2-day, adsorption	0.005	-0.012	0.994
R-S, 0.15-0.5 mm, soil NDOM, 4-day, adsorption	0.004	-0.015	0.994
R-S, 0.15-0.5 mm, soil NDOM, 2-day, adsorption	0.003	-0.009	0.995
R-O, <0.15 mm, soil NDOM, 4-day, adsorption	0.002	-0.003	0.995
R-O, <0.15 mm, soil NDOM, 2-day, adsorption	0.002	-0.016	0.999
R-O, 0.15-0.5 mm, soil NDOM, 4-day, adsorption	0.001	-0.005	0.996
R-O, 0.15-0.5 mm, soil NDOM, 2-day, adsorption	0.001	-0.008	0.993
C-H, 0.15-0.5 mm, stream NDOM, 2-day, adsorption	0.012	-0.033	0.991
C-S, 0.15-0.5 mm, stream NDOM, 2-day, adsorption	0.011	-0.061	0.942
C-O, 0.15-0.5 mm, stream NDOM, 2-day, adsorption	0.013	-0.153	0.977
C-A, 0.15-0.5 mm, stream NDOM, 2-day, adsorption	0.005	-0.050	0.432
R-S, <0.15 mm, soil NDOM, 4-day, desorption	0.005	0.004	1.000
R-S, 0.15-0.5 mm, soil NDOM, 4-day, desorption	0.003	0.004	1.000

a. Treatment listed as sorbent type, particle size, sorbate type, interaction time period, and experimental stage.

b. k_D is the slope (distribution coefficient) for linear model (L/g sorbent).

c. b is the y-axis intercept of the linear model (mg C/g sorbent).

Table 4-2. Linear model parameters (surface area-normalized)

Experimental treatment ^a	k_D ^b	b ^c	R^2
R-S, <0.15 mm, soil NDOM, 4-day	0.002	-0.003	0.997
R-S, <0.15 mm, soil NDOM, 2-day	0.001	-0.003	0.994
R-S, 0.15-0.5 mm, soil NDOM, 4-day	0.002	-0.006	0.994
R-S, 0.15-0.5 mm, soil NDOM, 2-day	0.001	-0.003	0.995
R-O, <0.15 mm, soil NDOM, 4-day	0.001	-0.002	0.995
R-O, <0.15 mm, soil NDOM, 2-day	0.001	-0.011	0.999
R-O, 0.15-0.5 mm, soil NDOM, 4-day	0.001	-0.010	0.993
R-O, 0.15-0.5 mm, soil NDOM, 2-day	0.001	-0.007	0.996
C-H, 0.15-0.5 mm, stream NDOM, 2-day	0.001	-0.003	0.991
C-S, 0.15-0.5 mm, stream NDOM, 2-day	0.003	-0.015	0.942
C-O, 0.15-0.5 mm, stream NDOM, 2-day	0.008	-0.092	0.977
C-A, 0.15-0.5 mm, stream NDOM, 2-day	0.011	-0.102	0.432

a. Treatment listed as sorbent type, particle size, sorbate type, and contact time period.

b. k_D is the slope (distribution coefficient) for linear model (L/m² sorbent).

c. b is the y-axis intercept of the linear model (mg C/m² sorbent).

Table 4-3. Amount NDOM adsorbed at two NDOM solution concentrations

Experimental treatment	5.00 mg C/L		20.00 mg C/L	
	NDOM adsorbed ^a (mg C/g sorbent)	% NDOM adsorbed	NDOM adsorbed (mg C/g sorbent)	% NDOM adsorbed
R-S, <0.15 mm, 4-day	0.014	44.1	0.089	67.2
R-S, <0.15 mm, 2-day	0.013	35.2	0.088	59.7
R-S, 0.15-0.5 mm, 4-day	0.005	18.6	0.065	59.7
R-S, 0.15-0.5 mm, 2-day	0.006	28.7	0.051	52.8
R-O, <0.15 mm, 4-day	0.007	51.0	0.037	64.4
R-O, <0.15 mm, 2-day	-0.006	-47.6	0.024	34.6
R-O, 0.15-0.5 mm, 4-day	0.000	-1.3	0.015	50.0
R-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	0.500	19.9

a. Calculated using linear isotherms listed in Table 4-1.

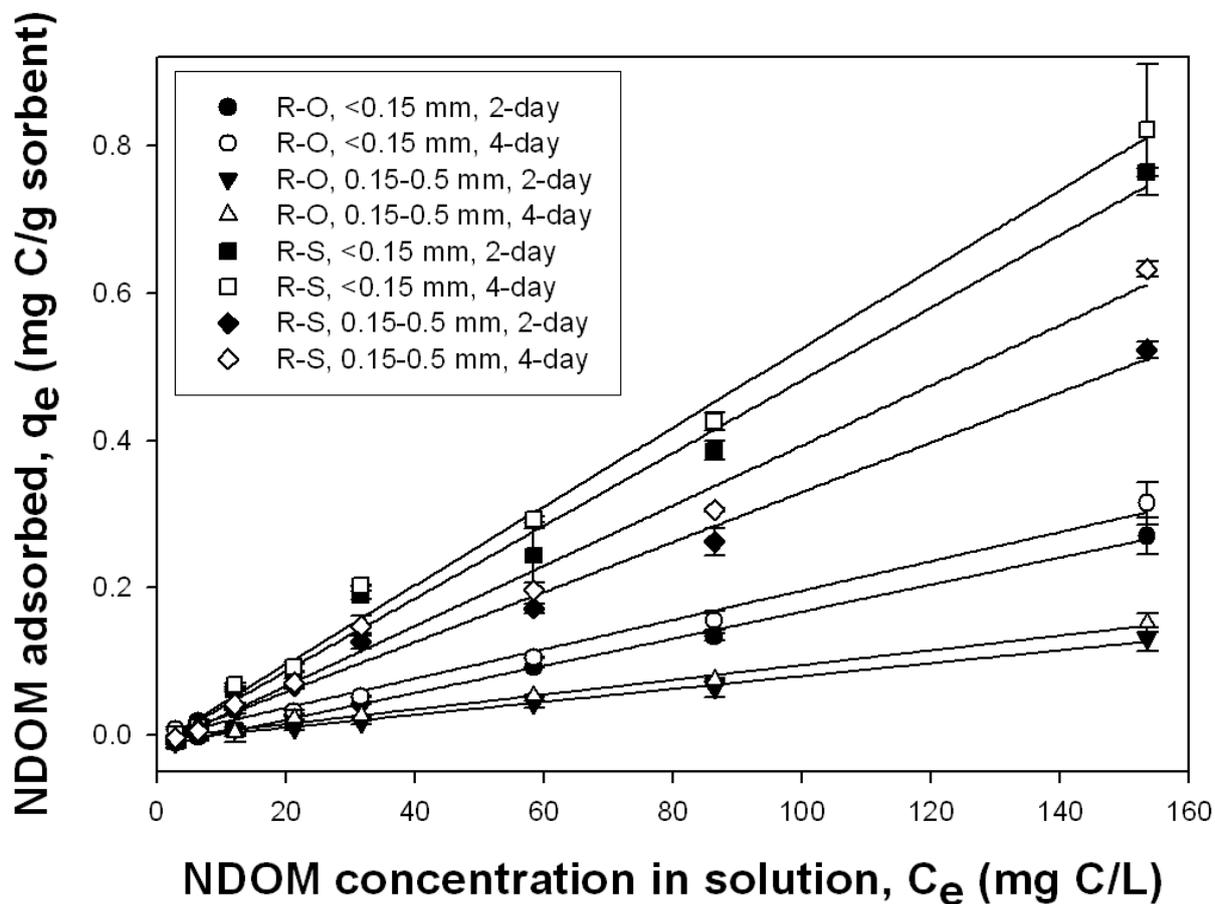


Figure 4-1. Adsorption data for soil NDOM on R-O and R-S carbonate rocks of two grain size fractions (<0.15 and 0.15-0.5 mm) and for 2 and 4 day interaction periods. Error bars represent the standard deviation of duplicate analyses. The solid lines are the linear model adsorption isotherms (details in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

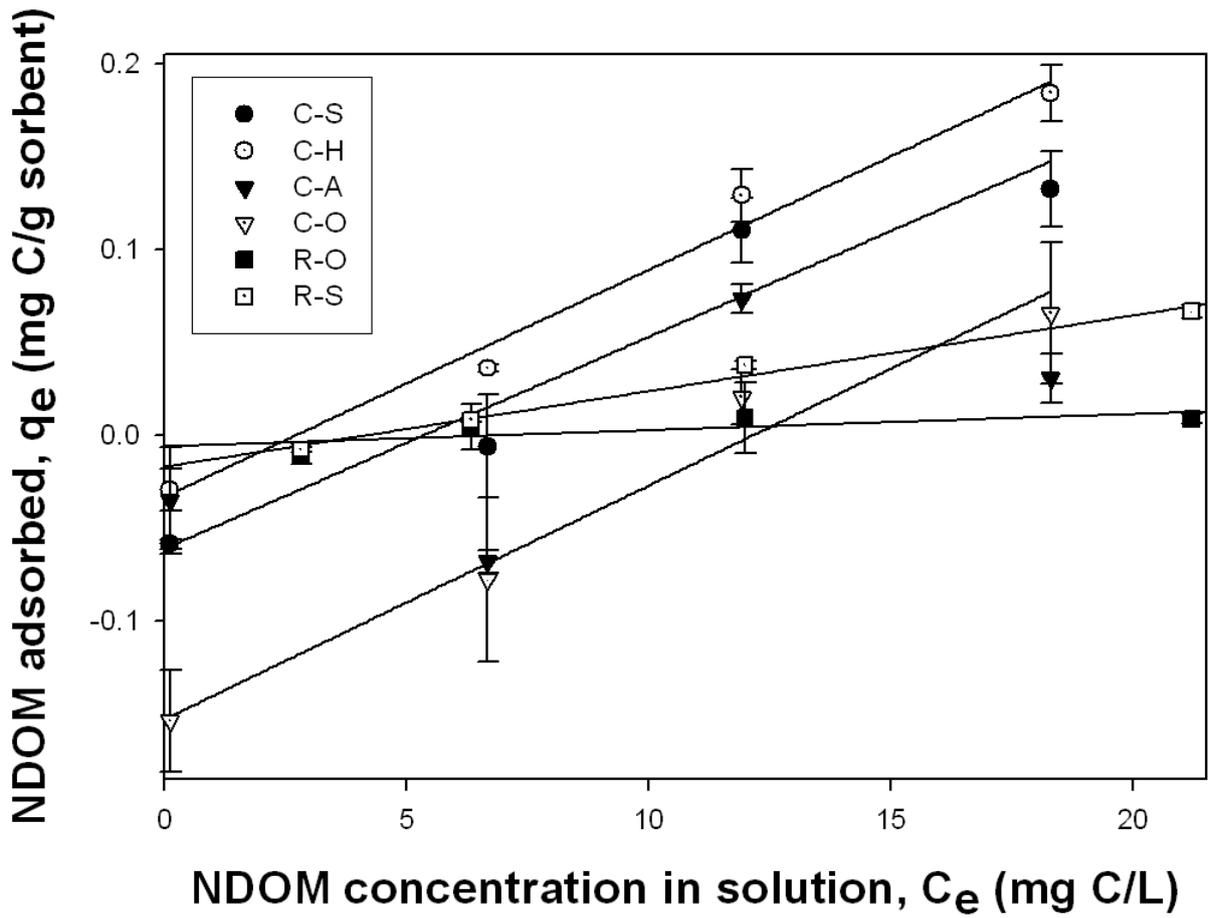


Figure 4-2. Adsorption data for stream NDOM on six carbonate sorbents (C-S, C-H, C-A, C-O, R-O and R-S). All the sorbents are of 0.15-0.5 mm grain size and adsorption time period is 2 days. Error bars represent the standard deviation of duplicate analyses. The solid lines are the linear model adsorption isotherms (details in text).

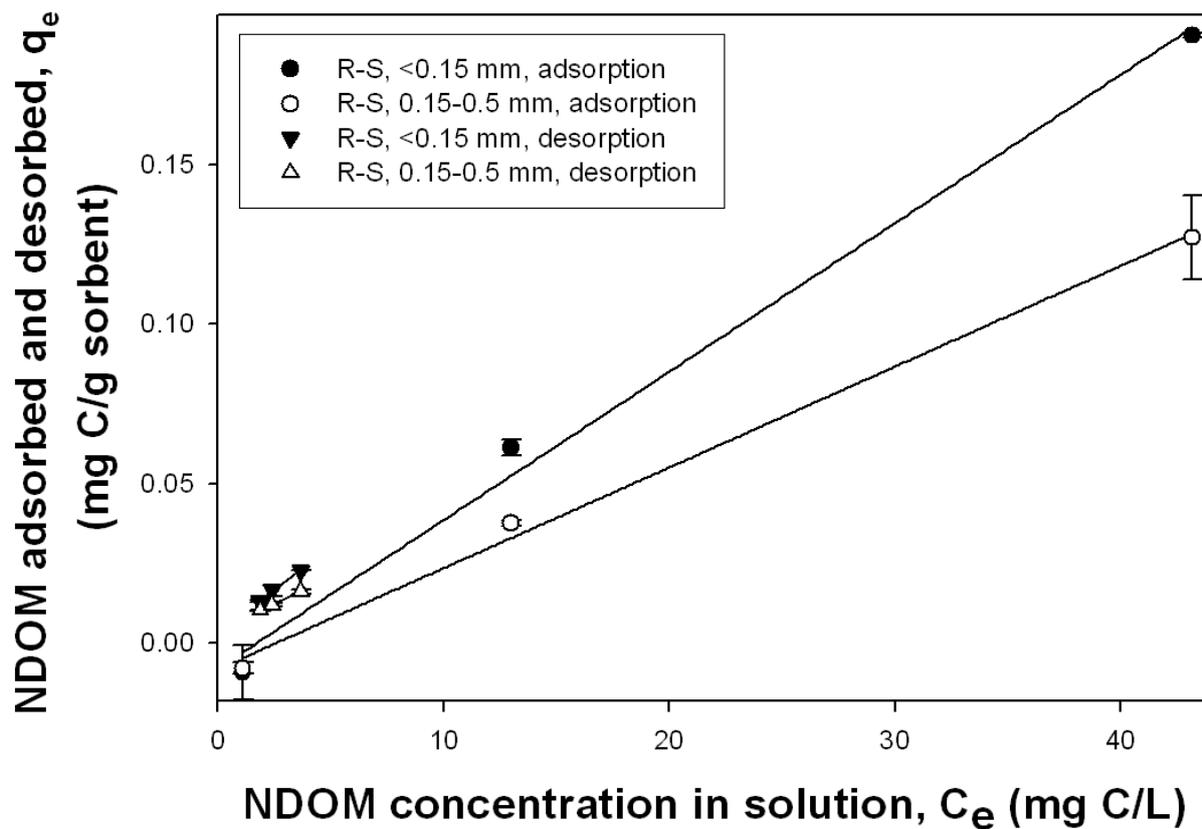


Figure 4-3. Adsorption and desorption data for soil NDOM on R-S of two grain sizes (<0.15 and 0.15-0.5 mm), 4-days. Error bars represent the standard deviation of duplicate analyses. The solid lines are the linear model fit of the adsorption and desorption isotherms (details in text).

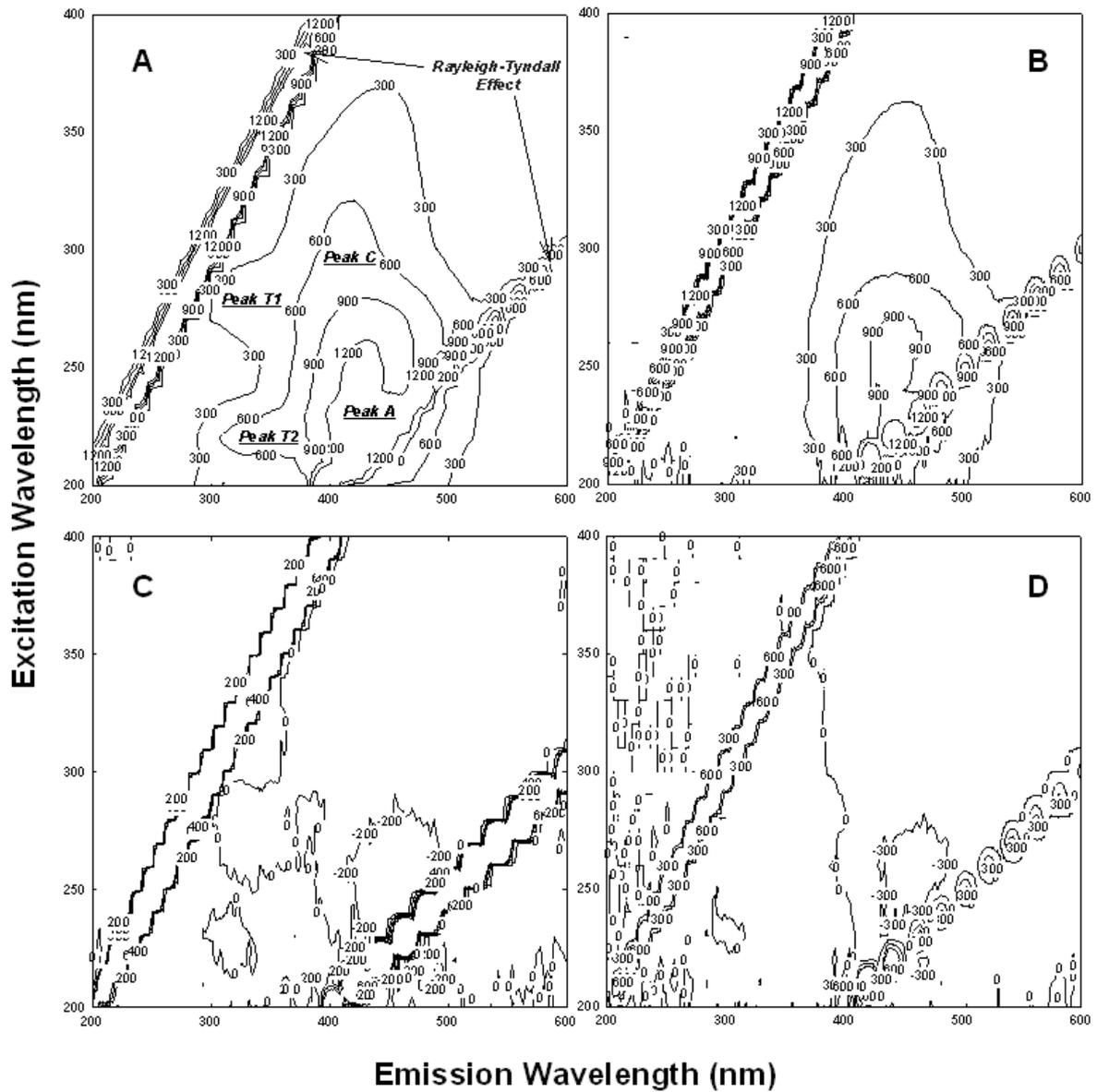


Figure 4-4. Excitation-emission matrices (EEM) of A) soil NDOM extracts illustrating position of fulvic-like (Peak C), humic-like (Peak A), and tryptophan-like (Peak T1 and T2) fluorophores, B) stream NDOM, C) preferential adsorption of humic-like fluorophores: supernatant EEM following 2-day interaction of carbonate rock (C-H, 0.15-0.5 mm) with soil NDOM (12.47 mg C/L) subtracted by starting supernatant EEM, D) preferential adsorption of humic-like fluorophores: following 2-day interaction of carbonate rock (C-H, 0.15-0.5 mm) with stream NDOM (18.19 mg C/L).

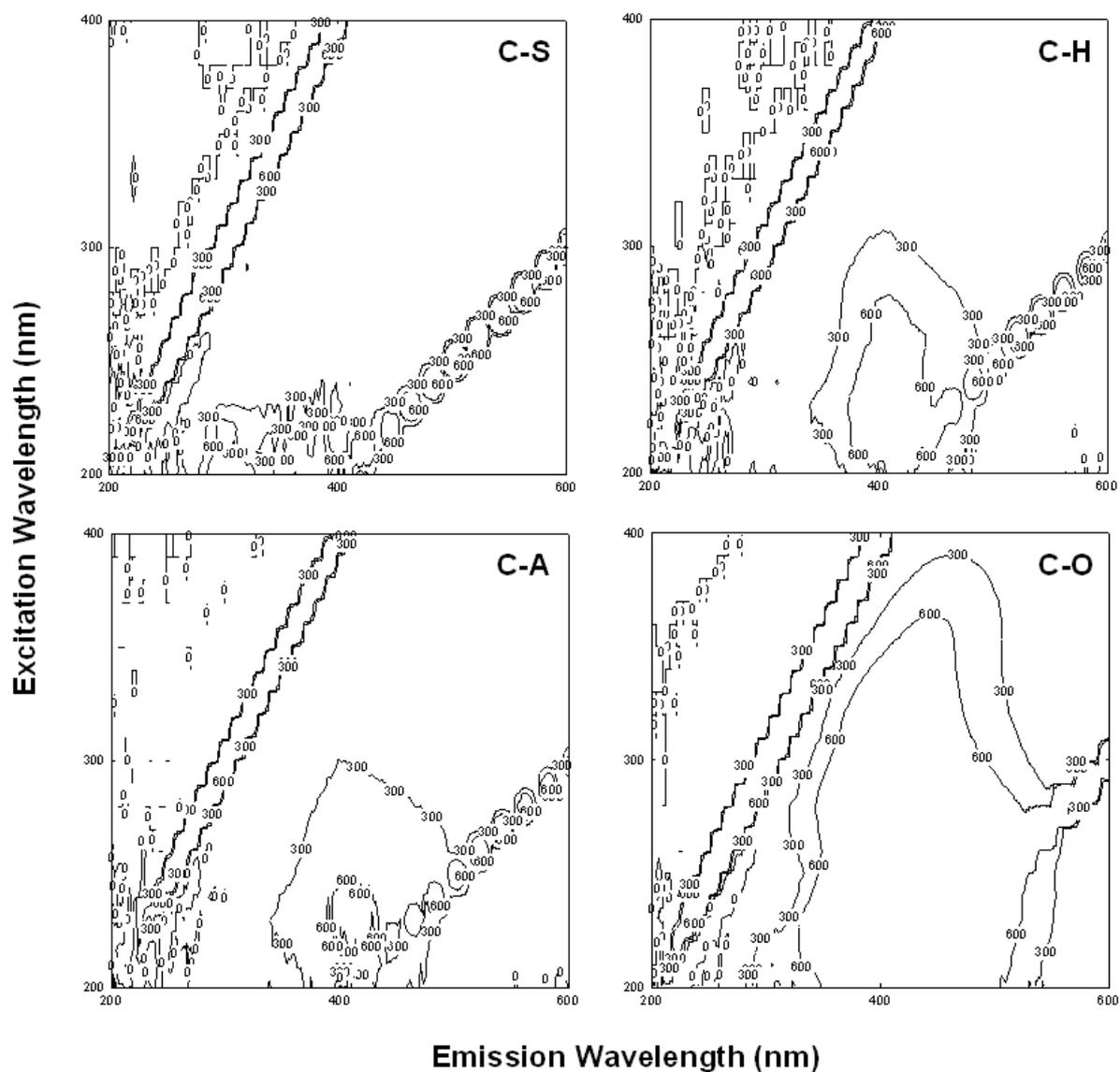


Figure 4-5. Excitation-emission matrices of indigenous organic matter released from aquifer core materials (C-S, C-H, C-A and C-O, all <0.15 mm) into water.

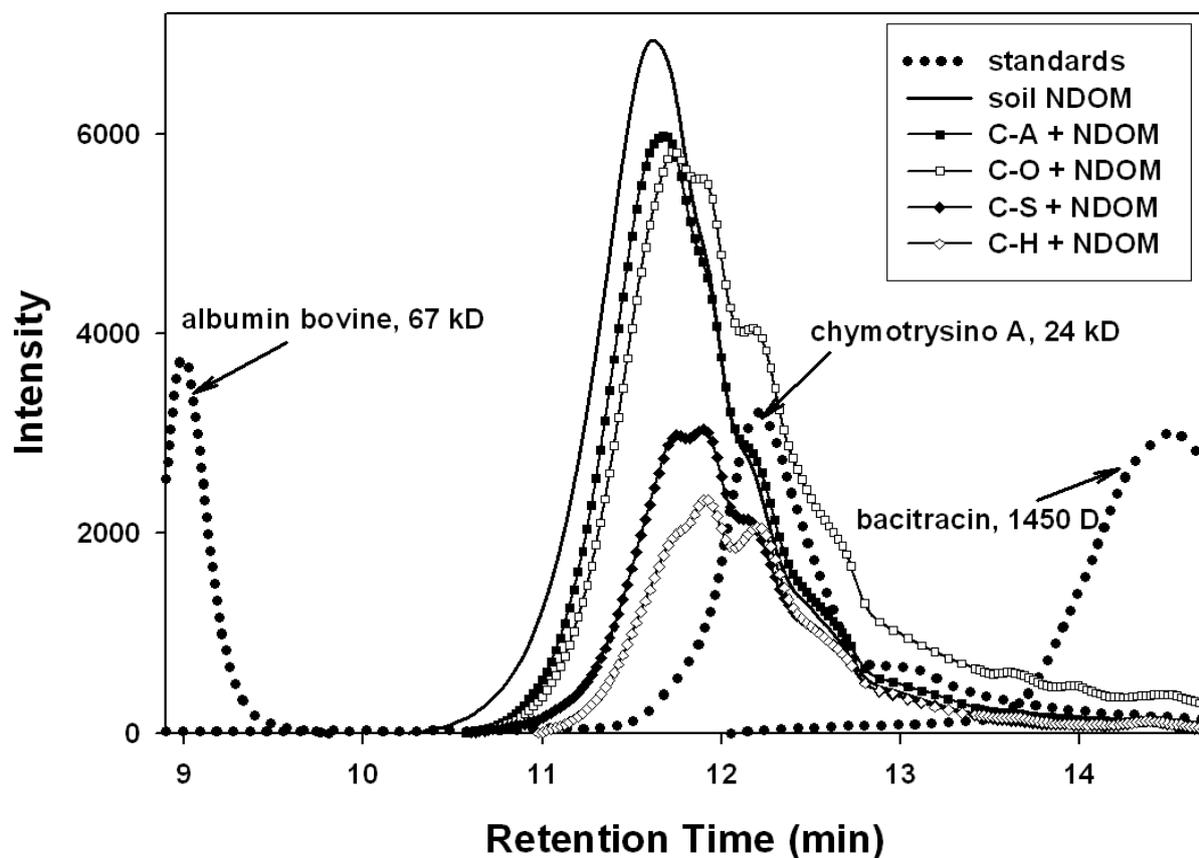


Figure 4-6. Liquid size exclusion chromatograph (HPLC-SEC) of soil NDOM (14.47 mg C/L) sorbate before and after interaction with four aquifer core materials (C-S, C-H, C-A and C-O, all 0.15-0.5 mm). Also shown are three protein molecular weight (M_w) standards (chymotrypsino A, $M_w=24$ kD; albumin bovine, 67 kD; bacitracin, 1450 D).

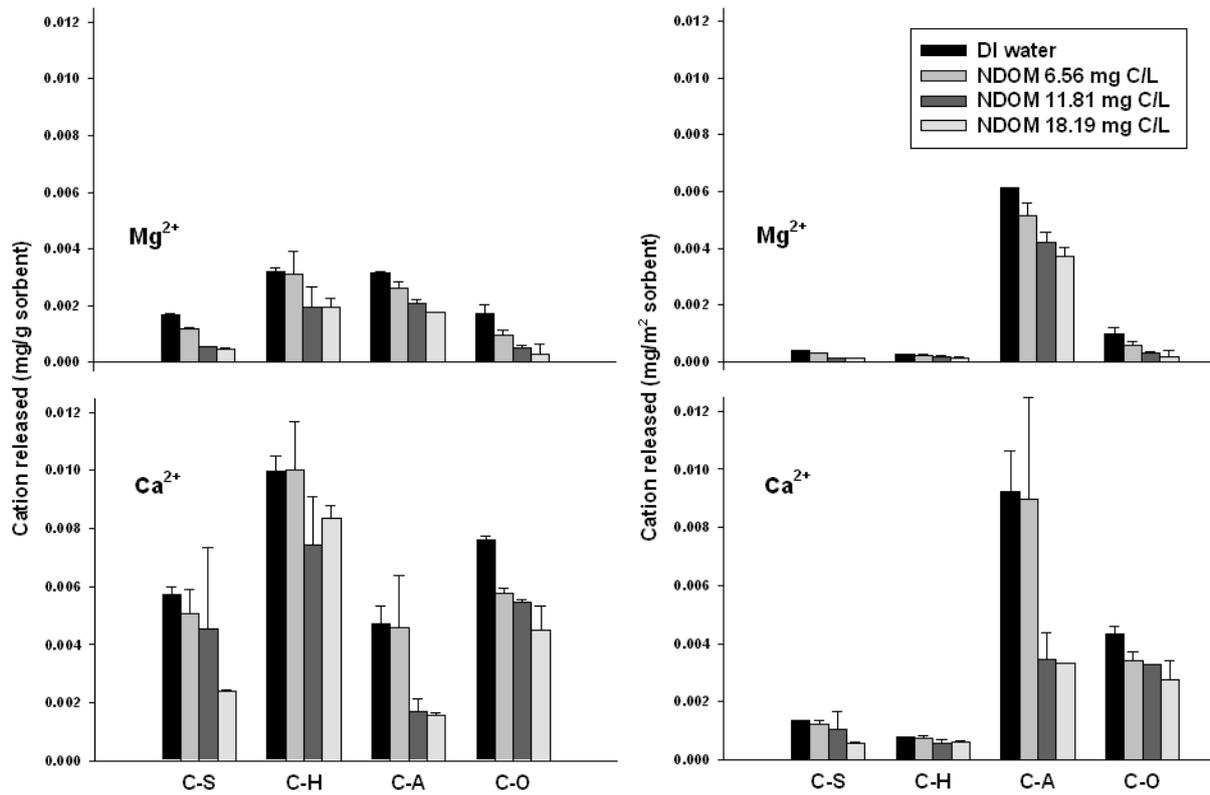


Figure 4-7. Ca^{2+} and Mg^{2+} released during 2-day interaction of distilled water and three concentrations of stream NDOM with aquifer core materials (C-S, C-H, C-A and C-O, all 0.15-0.5 mm). Left: Cations released normalized to sorbent weight (mg/g sorbent), right: Cations released normalized to sorbent surface area (mg/m² sorbent).

CHAPTER 5 DISCUSSION

The results of NDOM-carbonate interaction experiments revealed significant adsorption of all NDOM types to all karst aquifer materials examined. While this adsorption occurred at all NDOM concentrations for the Floridan Aquifer rock samples tested, release (desorption) of indigenous OM from the aquifer core sample tested occurred within the lower portion of the natural range of NDOM concentrations (<10 mg C/L). However, at higher NDOM concentrations, NDOM adsorption to the core materials occurred with an even greater affinity than that of the aquifer rock materials. For example, based on our linear adsorption model, at a commonly measured groundwater NDOM concentration (5 mg C/L), most of core materials as well as R-O showed negative values in both amount and percentage of NDOM adsorbed indicating the release of indigenous OM from the sorbents (Table 4-3). However, at a higher groundwater NDOM concentration level (e.g., 20 mg C/L) such as might be measured after a major precipitation event, all sorbents adsorbed NDOM (20-72% of that originally present in solution). A better understanding of the factors producing these trends can be obtained through an examination of the relationships between adsorption behavior and the characteristics of the aquifer sorbents tested.

Factors Controlling Karst Aquifer NDOM Adsorption

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, our 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 our study contain, in addition to calcite and/or dolomite (and quartz in the case of Hawthorn and Suwannee Fm. materials), variable amounts of apatite, metal oxides, clay, and even OM. It is unsurprising, therefore, that the more mineralogically homogeneous aquifer rocks produce highly linear isotherms, while those of the aquifer core materials contain 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 thought of as composed of a superposition 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 (Schwarzenbach *et al.*, 2003a). In our experiments, that appears to be humic acids and calcite.

Adsorption data for NDOM interaction with carbonate are well-fit using a linear model, which is commonly associated with the adsorption of nonionic, non-polar, and hydrophobic organic compounds via weak, physical forces such as van der Waals attraction (partition theory, Essington, 2004b). 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, there is no dividing line separating hydrophobic from hydrophilic compounds in NDOM, nor fast rule to dictate which isotherm model should apply to each. However, accurate as partition theory may be to describe the sorption behavior of hydrophobic NDOM, it has its limitation when dealing with our NDOM-carbonate adsorption system. On the one hand, it fails to elucidate the sorption mechanism for polar, ionic and hydrophilic fraction of NDOM, whose isotherms are not linear over broad concentration ranges. On the other hand, the partition theory generally refers to an

absorption rather than an adsorption mechanism. This may be applicable if OM is the primary sorbent in aquifer materials but not, generally, for minerals without significant microporosity.

Sorbent characteristics: Certainly, the physical and chemical property of carbonate aquifer sorbent materials is another factor likely to control adsorption. The contrasting character of the aquifer rock versus core materials make an interesting comparison in regards to their sorbent behavior. Though not determined, we can assume the aquifer rocks are of the same mineralogical composition as their core counterparts (i.e. from same geologic formation). Yet the rock materials are massive, unfractured and relatively light-color relative to the more friable and tan-colored core materials. The latter is likely to have seen greater groundwater, NDOM and microbial interaction resulting in alteration and addition of minor impurities such as secondary minerals, indigenous OM and metal oxides. While each may have considerable macroporosity, the core materials are likely much more permeable, and so, may be better representatives of the aquifer materials likely have the greatest chance of chemically interacting with groundwater, and thus, affect 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. No significant correlation was found between NDOM adsorption affinity (k_D) and the surface area of the six carbonate sorbents ($R^2=0.774$, p value of the slope=0.163). However, an excellent linear correlation is found between k_D and surface area for the aquifer rock samples alone (Figure 5-1, $R^2=0.990$, $p=0.023$). No such correlation was found among the core materials, alone (Figure 5-1, $R^2=0.933$, $p=0.543$), though all but the Avon Park Fm. core sample displayed roughly twice the adsorption affinity of their rock counterparts.

One can conclude, therefore, that surface area may be a controlling factor of adsorption for relatively pure carbonate samples, but not when other impurities are present.

Another possible controlling factor 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 non-polar and nonionic NDOM via hydrogen bonding. Adsorption of organic molecules onto carbonate surfaces requires displacing the water molecules at such a surface, which is quite 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.*, 2003b). Previous studies found OM can bind with other organic compounds (Amiri *et al.*, 2005; Chen *et al.*, 2005; Chen & Xing, 2005), and the organic coatings may also render hydrophilic surfaces hydrophobic and more capable of sorbing organic contaminants (McCarthy & Zachara, 1989; Murphy *et al.*, 1990). We should expect, therefore, that NDOM shows greater adsorption affinity for sorbents with more indigenous OM. A moderately strong linear correlation was found between the amount of indigenous OM in each sorbents and k_D (Figure 5-2, $R^2=0.868$, $p=0.101$). Though only significant to the 90% level of confidence, considering the other known or unknown impurities in the sorbents that could affect this relationship (and surface area as discussed previously), it is still reasonable to conclude that the presence of indigenous OM strongly influences NDOM adsorption.

Adsorption kinetics: Long-term adsorption of humic acid to calcite (Lee *et al.*, 2005), as well as to metal oxide (Gu *et al.*, 1994), was described as largely irreversible, and was attributed to ligand exchange and inner-sphere-like interactions (Gu *et al.*, 1994; Murphy *et al.*, 1990).

However, for environmental processes, it is, perhaps, inappropriate to model adsorption reactions as either completely reversible or completely irreversible (discussed here, Ditoro & Horzempa, 1982) and not all are in complete agreement as to the predominant OM-mineral adsorption mechanism (discussed in next sections). It was suggested that the adsorption process may be made up of a rapid and reversible initial stage followed by a much slower nonreversible stage (i.e. kinetically biphasic, Selim *et al.*, 1992; Vaccari & 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, we posit that the bonds formed during the 2 and 4-day experiments conducted in our 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 said that adsorption equilibrium was not achieved. For instance, at a 5 mg C/L background NDOM concentration, R-S (<0.15 mm) showed an increase of 8.9% in NDOM adsorption after 4- relative to 2-days, while there was an 14.7% increase for R-O (0.15-0.5 mm) at 20 mg C/L (Table 4-3). However, the increase was most apparent at higher NDOM concentration (>60 mg C/L), much higher than likely to be found in aquifers. By comparison, a previous study reported that SRHA adsorption to calcite was rapid, reaching equilibrium within in one day (Lee *et al.*, 2005). In contrast, the non-equilibrium found here in our 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.

OM-mineral sorption systems were shown to reach equilibrium in timescales ranging from a few minutes to years (Avena & Koopal, 1999; Ball & Roberts, 1991a; Day *et al.*, 1994;

Gu *et al.*, 1995; Gu *et al.*, 1994; Kleineidam *et al.*, 2004; Ochs *et al.*, 1994; Rugner *et al.*, 1999; Zhou *et al.*, 2001). For example, Zhou *et al.* (2001) reported that a fulvic-goethite adsorption system reached steady-state in about six hours. In contrast, no sorption equilibrium was found in an adsorption system of phenanthrene and aquifer materials (mineral separates from sandy aquifer sediments and fresh rock fragments) 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 & Roberts, 1991b; Grathwohl & Reinhard, 1993; Werth *et al.*, 2000), which is not applicable to our study (discussed further below). More recently, slowly reached equilibrium was attributed to a high sorption capacity (Kleineidam *et al.*, 2004). The carbonate system may be similar in that the linear isotherm displayed no evidence of reaching maximal adsorption capacity at the study conditions. However, from a thermodynamic perspective, all sorption system must, eventually, reach maximum adsorption capacity given either high enough NDOM concentration or long enough interaction time, or both.

Adsorption/desorption mechanism: 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 our 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 concentration,

adsorption would become more and more difficult until all the sites are occupied (when $k_D=0$). Others have also reported that different isotherm models apply to different sorbate concentration ranges (Lee *et al.*, 2005; Murphy *et al.*, 1992; Murphy *et al.*, 1990). For example, Lee *et al.* (2005) found that a SRHA-calcite adsorption system showed Langmuir behavior at low concentrations (0-15 mg C/L) and non-Langmuir behavior at higher concentrations. The reason for such change in adsorption behavior was attributed to (1) a change of NDOM molecular orientation at the sorbent surface (Lu & Miller, 2002), (2) mutual interactions between sorbate molecules which enhances the adsorption affinity at higher loadings (Sposito, 1984), and (3) aggregation of NDOM on the sorbent surface as background concentration increases (Namjesnik-Dejanovic *et al.*, 2000).

During the desorption experimental stage, when background NDOM solution concentration was lowered, most, but not all of the adsorbed NDOM was released (e.g., 73-88% desorption for C-S), indicating that the NDOM-carbonate rock system, though close to reversible, had some hysteresis. However, factors other than true irreversible adsorption, can cause hysteresis, such as experimental artifacts, inappropriate experimental design, and non-equilibrium of either the adsorption or desorption process. Given that the adsorption leg is 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 may be that the hysteresis is a false one. However, a signal that desorption equilibrium was reached is the near equivalence of the desorption and adsorption k_D (isotherm slope) (Essington, 2004c). For the 4-day adsorption and desorption stage of R-S (<0.15 mm) with soil NDOM, both k_D values were found to be 0.005, while for R-S (0.15-0.5 mm), adsorption k_D (0.004) and desorption k_D (0.003) were very similar (Table 4-1). In addition, considering the hydrophobic interaction between our

sorbates and sorbents (e.g., preferential adsorption of hydrophobic fraction of NDOM, discussed later), which would cause hysteresis, would lead to the conclusion that the NDOM-carbonate system is not completely reversible.

Observations of the preferential adsorption of acidic organic compounds and an accompanying pH increase in background solution has led to ligand exchange to be a proposed adsorption mechanism OM adsorption onto calcite (Carter & Mitterer, 1978) and iron oxide (Tipping, 1981). Ligand exchange is not likely the primary adsorption mechanism occurring in our system, as no pH change was detected. However, considering that the carbonate mineral provide a strong pH buffer, the change in pH (reflecting the extent of ligand exchange) might be too small to be detected. Conformational changes in certain NDOM functional groups (e.g., –COOH and –OH) during hydrophobic interaction between NDOM and sorbents, is also able to give a good explanation for little acidity change during adsorption (Avena & Koopal, 1999; Davis, 1982; Geffroy *et al.*, 2000). On the other hand, the transformation of carbonate surface from hydrophilic to hydrophobic, (e.g., incorporating indigenous OM or forming organic coating via prior sorption), also facilitates the hydrophobic interaction.

We propose 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. However, at longer time intervals, the stronger hydrophobic interactions occur, creates irreversibility and the observed desorption hysteresis.

NDOM Transformation due to Abiotic Carbonate Interaction

Our observation of preferential adsorption of a high over low M_w NDOM, and a humic-like over fulvic-like fraction onto carbonate sorbents is in agreement with the findings of other

published studies. For example, the higher M_w and hydrophobic fraction of Suwannee River fulvic acid (SRFA) standard were preferentially adsorbed, relative to lower M_w and hydrophilic fractions, to both kaolinite and hematite (Hur & Schlautman, 2003). Similar results were reported in studies of bulk NDOM adsorption to various clay and metal oxide sorbents (Gu *et al.*, 1994; Meier *et al.*, 1999). Kaiser (2003) also found such preferential adsorption in a NDOM-synthetic goethite adsorption system and concluded that strong sorption of the hydrophobic fractions may be caused by the presence of aromatic structures. It was hypothesized that hydrophobic effects, and to a lesser extent, ligand exchange, were the dominant mechanisms contributing to the preferential adsorption of SRFA and SRHA onto both synthetic and natural aquifer materials (Chi & Amy, 2004). Preferential adsorption of humic-like over fulvic-like compounds shown in our study (Figure 4-4c. and d.) also agrees with observations that post-mineral-interacted NDOM is likely to contain more fulvic acid than humic acid (Hedges & Oades, 1997). The preferential adsorption patterns observed in our systems were similar to those of other mineral oxides systems. Therefore, in aquifer systems, the aromaticity of NDOM is likely to be an important determinant for preferential adsorption of hydrophobic and humic-like fraction of NDOM. This can well explained by adsorption mechanism that we proposed earlier. During the slow hydrophobic interaction stages, high over low M_w NDOM are preferentially adsorbed, and thus lead to sorption hysteresis.

The indigenous OM detected in the aquifer materials may have both altered NDOM composition and sorbent surface chemistry, and thus influenced the adsorption process. Indigenous OM released from the carbonate sorbents was most apparent at low NDOM solution concentrations and among the core sorbent materials. Little OM release from aquifer rocks was observed, which was not surprising given their very low OC contents (Table 3-2). 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 four core materials, had the weakest tendency to release OM into solution, while C-O released the most OC. This indicates that the type and OM-mineral association of indigenous OM in each aquifer material is not likely the same. Other sorbent chemical parameters (such as surface area, elemental composition, adsorption affinity, or cations released to solution via dissolution) were also not found to be clearly related to OM release. We conclude 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 results showed that indigenous OM released from carbonate samples generally contained humic-like substances (peak A), except for C-O, which contains both humic-like and fulvic-like substances (Figure 4-5). In addition, HPLC-SEC M_w distributions showed indigenous OM of both core materials and aquifer rocks 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, see Appendix V), distinct from the NDOM peaks (average M_w =30.6 kD). Considering both EEM and HPLC results, we conclude that, although the main composition of indigenous OM may be categorized as humic-like substances, similar to that found in soil and stream NDOM, the indigenous OM also contains both larger and smaller M_w compounds that may be easily released when background NDOM concentrations are low, should fresh surfaces be exposed due to, for example, dissolution. The direct observation of these indigenous OM peaks (HPLC data) in the post-interacted background solution further confirms the exchange of OM between the aqueous and

solid phases. The origin of this indigenous OM is not known, but a likely source is 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.

NDOM Effect on Carbonate Dissolution

Though microbial conversion of OC to inorganic C should increase the rate of carbonate dissolution (Perry *et al.*, 2003; Perry *et al.*, 2004), it is likely this effect was small to absent in our experiment because samples were treated aseptically and the 2-day interaction period allowed little time for microbial acclimatization to the OC source. Thus, release of Ca^{2+} and Mg^{2+} cations into solution (final - starting cation concentration in supernatant), which we attribute to mineral dissolution, is likely due wholly to abiotic hydrolyzation of mineral surfaces. On a weight-normalized basis, C-H had the greatest dissolution tendency and C-A least. However, on a surface area-normalized basis the trend was just the opposite. This is likely because the higher surface area of C-H is due to clays which do not release cations. Although surface area may have been a contributing factor in determining dissolution extent, mineralogy played a more important role.

Dolomite, the main constituent of C-A, has a much smaller solubility product than calcite, the dominant mineral of the other three core materials (at 25°C, $K_{\text{calcite}}=10^{-8.48}$, $K_{\text{dolomite}}=10^{-17.2}$ Drever, 2002c). This is reflected in our results that C-A released least amount of Ca^{2+} in DI water on a weight normalized basis. C-S showed smaller Mg^{2+} and Ca^{2+} release than C-O, likely due to the presence of quartz in C-S which correspondingly lowered its calcite content. For the relatively high cation release from C-H, though it contains significant quartz, may be due to the high solubility of apatite.

In general, the presence of NDOM inhibited mineral dissolution, but the dissolution inhibition observed was not always proportional to NDOM solution concentration. For example, no or only a small amount of inhibition occurred at 6.6 mg C/L NDOM (the concentration at which little NDOM adsorption occurs). There is only a small difference 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 is due to protection of mineral surface by organic coating, and not to organic complexation of cations in solution. Though the issue of whether the presence of OM inhibit or enhance carbonate dissolution is still being debated, our conclusion is supported by many previous studies. Thomas et al (Thomas *et al.*, 1993) reported that organic compounds that adsorb strongly onto calcite and dolomite (fatty acids and carboxylated polymers) inhibited dissolution, while weak adsorbates and non-adsorbates showed little or no effect on the dissolution rates. Phillips et al (2005) reported that citrate molecules in a solution of precipitating calcite are incorporated structurally into the calcite crystal, and suggested that water and hydrogen-bonding interactions plays a role in the organic molecules-calcite interface.

Lastly, it is noticed that, for each of the four core materials, the dissolution indicated by Ca^{2+} release is not the same as Mg^{2+} . For example, the order of the extent of dissolution inhibition indicated by of Ca^{+2} among four sorbents at the highest NDOM concentration (18.19 mg C/L) is: C-A (66%) > C-S (58%) > C-O (41%) > C-H (16%), while for Mg^{2+} , it is: C-O (82%) > C-S (73%) > C-A (45%) > C-H (39%). This asynchronous dissolution inhibition 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) must have been relatively more protected by NDOM coverage.

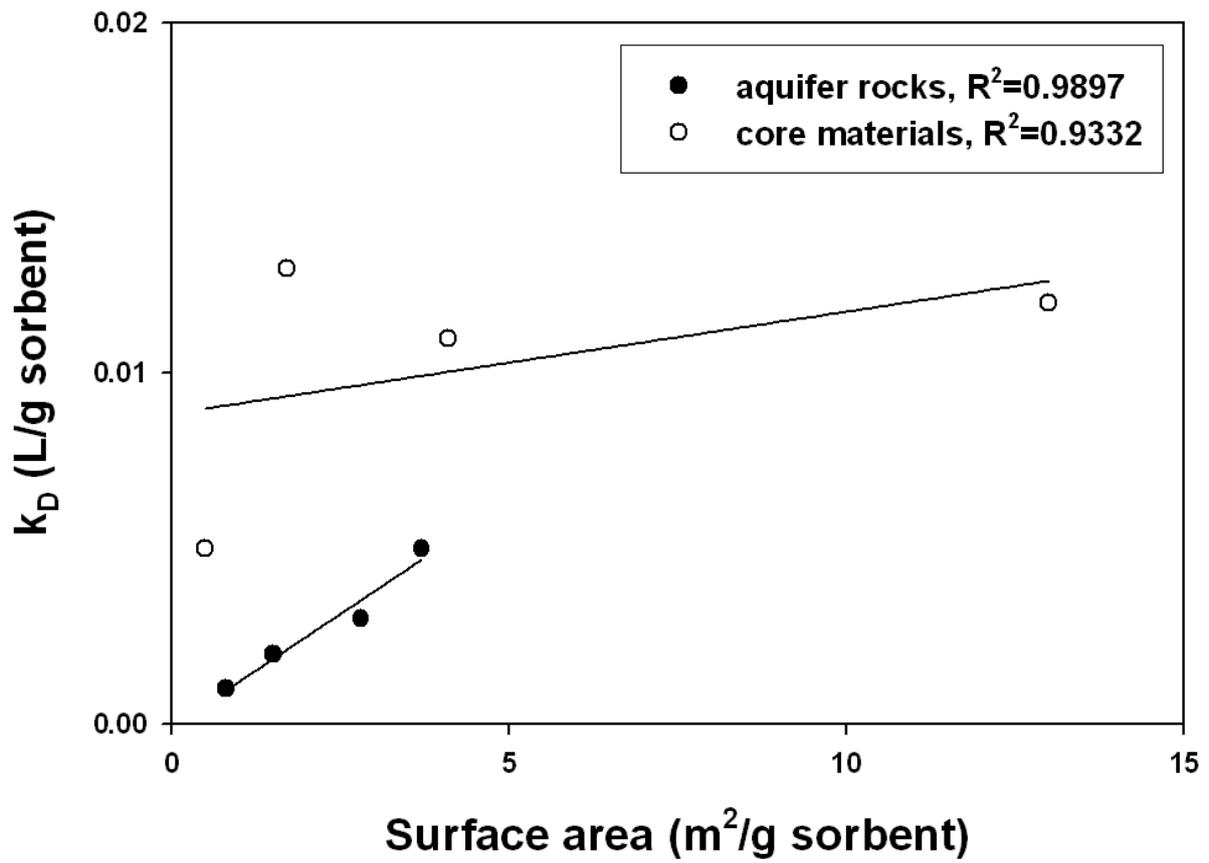


Figure 5-1. Plot of sorbent surface area (m²/g sorbent) versus adsorption affinity (L/g sorbent) for six Floridan Aquifer materials.

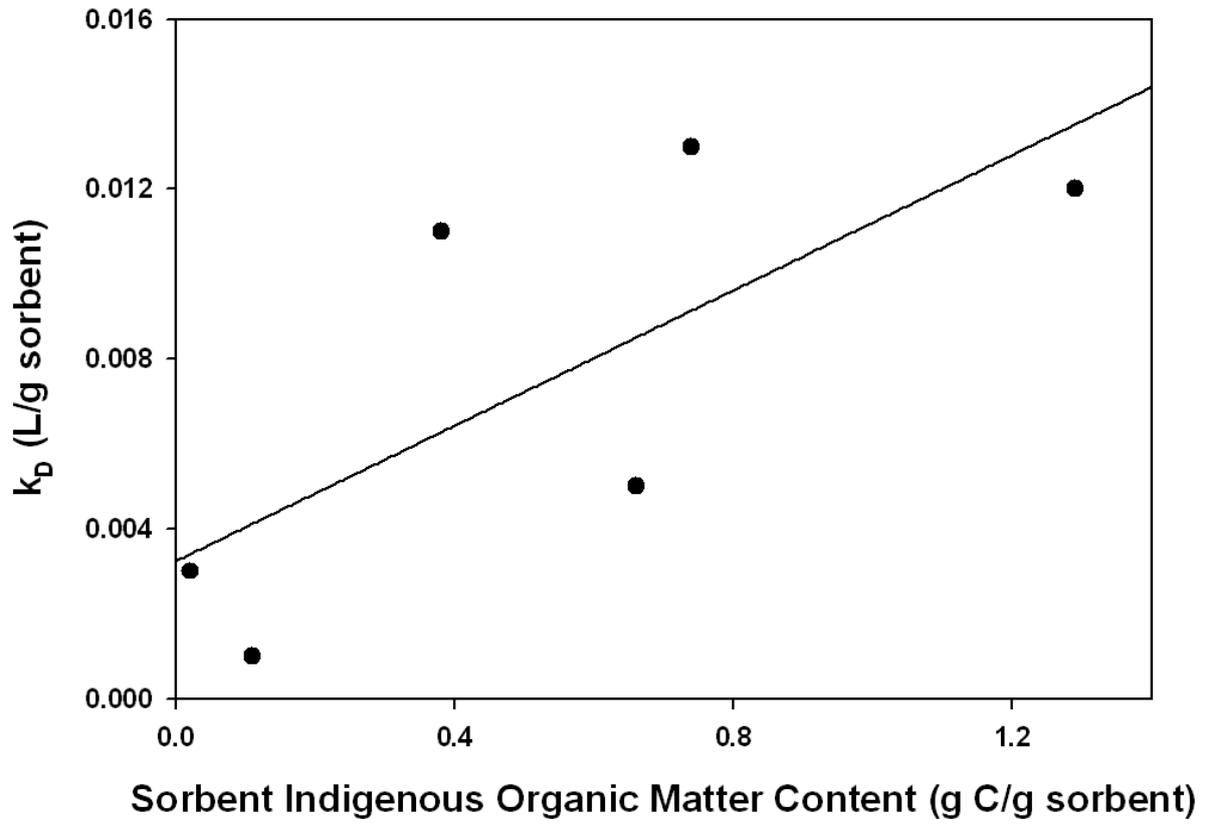


Figure 5-2. Plot of sorbent indigenous organic matter content (g C/g sorbent) versus adsorption affinity (L/g sorbent) for six Floridan Aquifer materials.

CHAPTER 6 AQUIFER ENVIRONMENTAL IMPLICATION AND CONCLUSION

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, and groundwater flow velocity all control the pace and extent of OM transference 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, the results presented here make clear the important role that abiotic factors can potentially play as well. Additionally, given its relatively greater surface connectivity and permeability, and, thus, variability in NDOM concentration and contact time, the effects of abiotic mineral interaction may be temporally and spatially variable. The results of our study show that, due to slow adsorption kinetics, longer groundwater retention or slower flow rates will lead to greater NDOM adsorption in a karst 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. These processes will be enhanced by the presence of indigenous OM which will have the tendency to be released during periods of low NDOM concentration and enhance NDOM adsorption when greater concentrations of NDOM are present.

Preferential adsorptions of some NDOM components onto carbonate minerals may modify the properties (e.g. electrostatic) of aquifer mineral surfaces and, thus, have an important effect on their subsequent sorption behavior. Almost all solid surfaces in natural groundwater systems are negatively charged due to organic coating (Gu *et al.*, 1994; Liang *et al.*, 1993; McCarthy *et al.*, 1993; McKnight *et al.*, 1992). Hence, positively charged organic compounds in

groundwater (e.g., amino acids and proteins) are readily removed by cation exchange, while hydrophilic neutral (e.g. carbohydrates and alcohols) and low M_w anionic OM (e.g. organic acids) are poorly retained by aquifer solids (Aiken, 2002). Preferential adsorption of humic acid-type to carbonate materials that we observed is also expected to affect groundwater quality as it can render the groundwater NDOM to be more hydrophilic. These OM components that are not adsorbed may be considered the more likely fuel for microbial metabolism and are, potentially, pollutants of greater concern in regards to drinking water quality. Further, the fate and transport of nutrients such as nitrates and phosphates, too, may be tied to that of NDOM. The adsorption of NDOM to aquifer minerals removes organic N and P forms and prevents 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 aquifer material of all types examined is inhibited by the presence of NDOM at all concentrations has environmental implications as well. The presence of NDOM in aquifers might be expected to prevent the mobilization of heavy metals, radio-nuclides and other constituents from the aquifer matrix into groundwater. However, biotic processes must also be considered such as the release of inorganic carbon by microbial mineralization of NDOM, which will enhance carbonate dissolution, and the coupling of NDOM reduction with the oxidation of reduced mineral forms, thus altering the solubility of metals and radio-nuclides. As enhanced carbonate dissolution in karstic areas leads to geological hazards such as land surface subsidence, it will be important to determine the relative influence of abiotic and biotic factors on carbonate dissolution when considering projects that may change to groundwater chemistry.

An improved understanding of the abiotic NDOM-carbonate interaction processes which may occur in karst aquifer systems may be of benefit when conducting hydrogeologic projects such as ASR and 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, our study has shown that water with all NDOM removed may have implications for groundwater chemistry as well. Clearly additional work should be carried out to examine both abiotic and biotic NDOM-mineral interactions simultaneously, such as incubations using native groundwater microbial populations. These experiments should be carried out in both batch and column modes, and, lastly field scale ‘ground-truthing’ studies should be carried out 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.

APPENDIX A DETAILS OF ANALYTICAL METHODS USED

HPLC: High-performance size exclusion chromatography (HPLC-SEC), also known as gel permeation chromatography or gel filtration chromatography, is often used to characterize the molecular weight distribution of NDOM due to its sensitivity and reproducibility (Wu, 2003). In addition, HPLC requires relatively small sample volumes, in many cases, without sample pre-concentration. With the careful use of standards, it reveals not only the molecular size distribution, but also the weight (M_w) and number (M_n) averaged molecular weight of a sample.

HPLC-SEC coupled with UV detection was commonly used to examine NDOM composition (e.g., Her *et al.*, 2003; Lepane, 2001; Lepane & Kudrjashova, 2001), reactivity (e.g., Namjesnik-Dejanovic *et al.*, 2000; Zhou *et al.*, 2001), as well as changes in molecular size distribution following adsorption reactions (e.g., Hur & Schlautman, 2003; Specht *et al.*, 2000).

In our study, the M_w distribution of NDOM before and after adsorption was determined by HPLC-SEC according to the methods of Chin (1994), modified by Zhou (2000). The SEC column was calibrated using four protein standards. Name, concentration, M_w of the four proteins used and their corresponding retention time are shown in Table A-1. Calibration function obtained by linear regression of the M_w versus Retention time of protein standards (Figure A-1).

EEM: Fluorescence is one possible outcome from molecular absorption of a quantum of light energy equal to the difference between two electron orbital levels. The native fluorescence characteristics of NDOM can be utilized as a sensitive and non-destructive means of investigating the composition, source and transformation of NDOM (Baker, 2005). Recent instrument advances in fluorescence spectrometer permit the rapid measurement of NDOM fluorescence properties at low concentration over a continuous range of both excitation and emission wavelengths (Coble, 1996) and requires only a small sample size (<5 ml) (Baker & Lamont-Black, 2001).

In our study, excitation-emission matrixes (EEM) of each NDOM-carbonate sorbent pair, both before and after 2-day interaction, were examined using a Hitachi F-7000 fluorescence spectrometer. Excitation wavelengths from 200 to 450 nm incremented at 10 nm intervals were collected. For each excitation wavelength, emission was measured from 200 to 700 nm at 3 nm intervals.

Table A-1. Calibration of the HPLC-SEC column

Standard Name	Concentration (ppm)	M _w (kD)	Retention Time (minute)
albumin bovine	220	67	9
ovalbumin	260	45	9.7
chymotrysinogen A	200	24	12.2
bacitracin	110	1.45	14.5

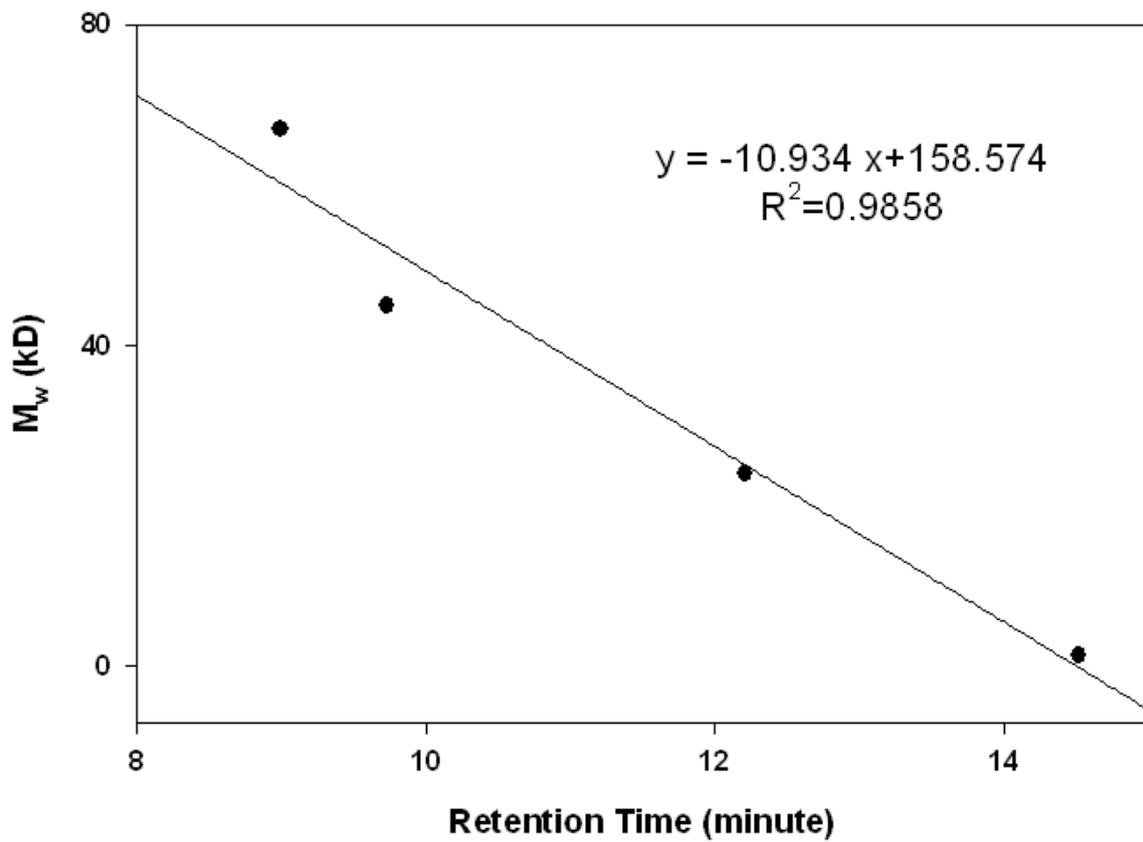


Figure A-1. HPLC-SEC column calibration function

APPENDIX B
FLORIDAN AQUIFER GEOLOGIC FRAMEWORK

SERIES	STRATIGRAPHIC UNIT	HYDROGEOLOGIC UNIT	
Miocene	<i>Hawthorn Group</i>	Intermediate Confining Unit	
Oligocene	<i>Suwannee Limestone</i>	Florida Aquifer System	Upper Florida Aquifer
Eocene	<i>Ocala Limestone</i>		
	<i>Avon Park Formation</i>		Middle Confining Unit
Paleocene	<i>Oldsmar & Cedar Keys Formations</i>		Lower Florida Aquifer

Figure B-1. Floridan Aquifer geologic framework (after Randazzo & Jones, 1997)

APPENDIX C
ALTERNATIVE ADSORPTION MODEL PARAMETERS

Table C-1. Langmuir Model ($q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e}$) Parameters (weight-normalized)

Experimental treatment	K_L (L/mg)	q_{\max} (mg/g)	R^2
R-S <0.15 mm, soil NDOM, 4-day	1.041E-08	5.126E+05	0.999
R-S <0.15 mm, soil NDOM, 2-day	1.661E-08	2.948E+05	0.997
R-S 0.15-0.5 mm, soil NDOM, 4-day	1.159E-08	3.446E+05	0.995
R-S 0.15-0.5 mm, soil NDOM, 2-day	1.702E-08	1.968E+05	0.997
R-O <0.15 mm, soil NDOM, 4-day	4.703E-08	4.295E+04	0.994
R-O <0.15 mm, soil NDOM, 2-day	3.446E-08	5.007E+04	0.994
R-O 0.15-0.5 mm, soil NDOM, 4-day	4.994E-08	1.955E+04	0.996
R-O 0.15-0.5 mm, soil NDOM, 2-day	6.960E-08	1.183E+04	0.989
C-H 0.15-0.5 mm, stream NDOM, 2-day	1.779E-03	6.958E+00	0.994
C-S 0.15-0.5 mm, stream NDOM, 2-day	9.843E-03	1.323E+00	0.973
C-O 0.15-0.5 mm, stream NDOM, 2-day	1.227E-02	1.236E+00	0.993
C-A 0.15-0.5 mm, stream NDOM, 2-day	1.769E-07	2.498E+04	0.583

Table C-2. Freundlich Model ($q_e = K_F C_e^n$) Parameters (weight-normalized)

Experimental treatment	K_F (L/g)	n	R^2
R-S <0.15 mm, soil NDOM, 4-day	0.004	1.063	0.999
R-S <0.15 mm, soil NDOM, 2-day	0.003	1.098	0.999
R-S 0.15-0.5 mm, soil NDOM, 4-day	0.002	1.150	0.999
R-S 0.15-0.5 mm, soil NDOM, 2-day	0.002	1.095	0.999
R-O <0.15 mm, soil NDOM, 4-day	0.001	1.077	0.995
R-O <0.15 mm, soil NDOM, 2-day	0.001	1.141	0.998
R-O 0.15-0.5 mm, soil NDOM, 4-day	0.001	1.082	0.997
R-O 0.15-0.5 mm, soil NDOM, 2-day	0.000	1.170	0.994
C-H 0.15-0.5 mm, stream NDOM, 2-day	0.012	1.013	0.994
C-S 0.15-0.5 mm, stream NDOM, 2-day	0.013	0.950	0.972
C-O 0.15-0.5 mm, stream NDOM, 2-day	0.017	0.900	0.992
C-A 0.15-0.5 mm, stream NDOM, 2-day	0.002	1.313	0.592

APPENDIX D
SORBENT X-RAY DIFFRACTION RESULTS

XRD measurements were conducted in Soil and Water Science Department, University of Florida by Dr. W. Harris. Results show that the C-A is nearly pure dolomite, the C-O is nearly pure calcite, C-H has calcite, dolomite, quartz, apatite, and palygorskite, and C-S is calcite and quartz.

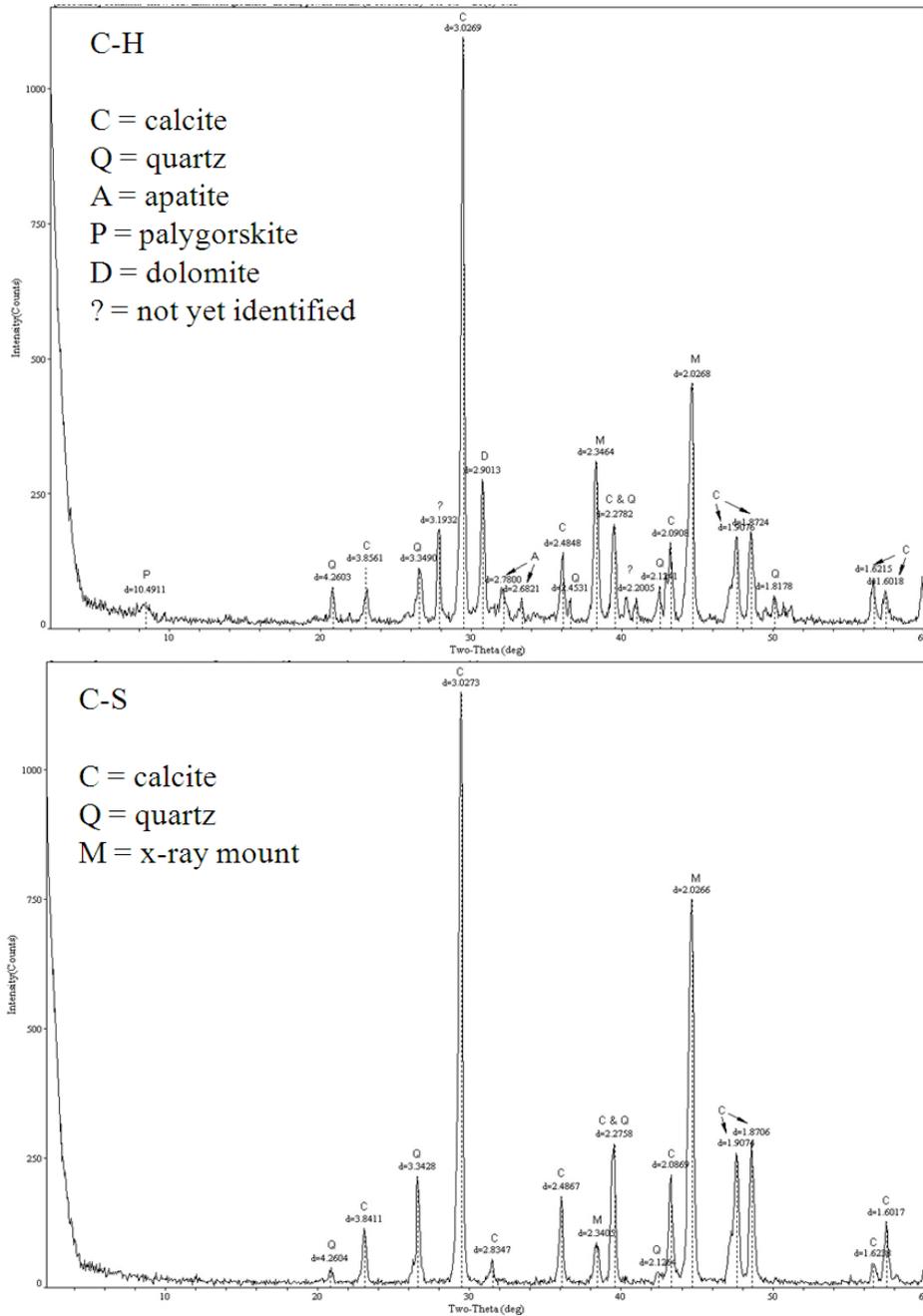


Figure D-1. Sorbent X-ray diffraction results

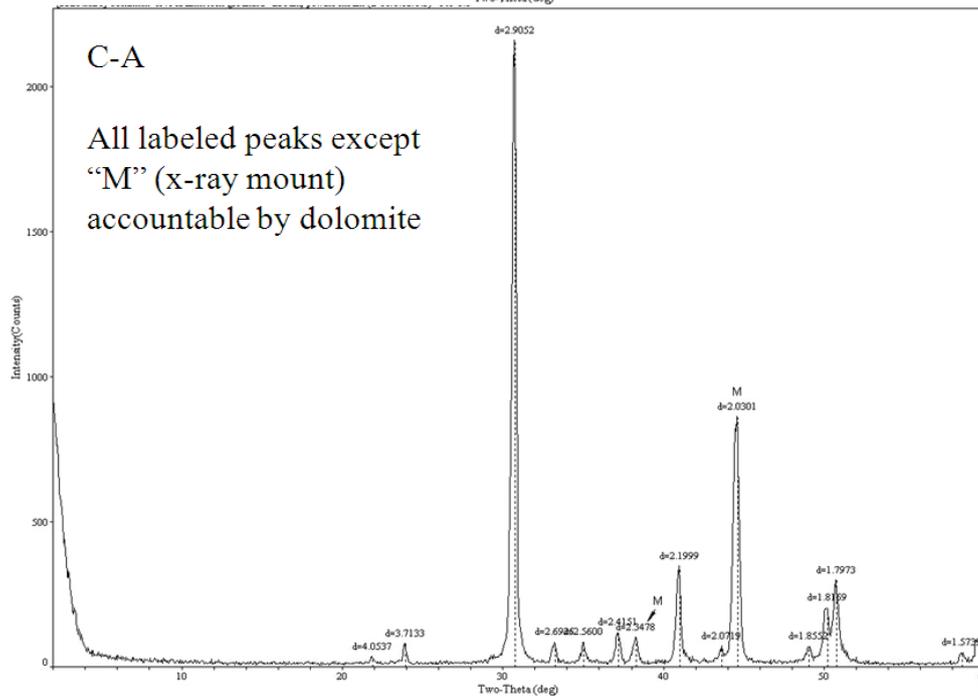
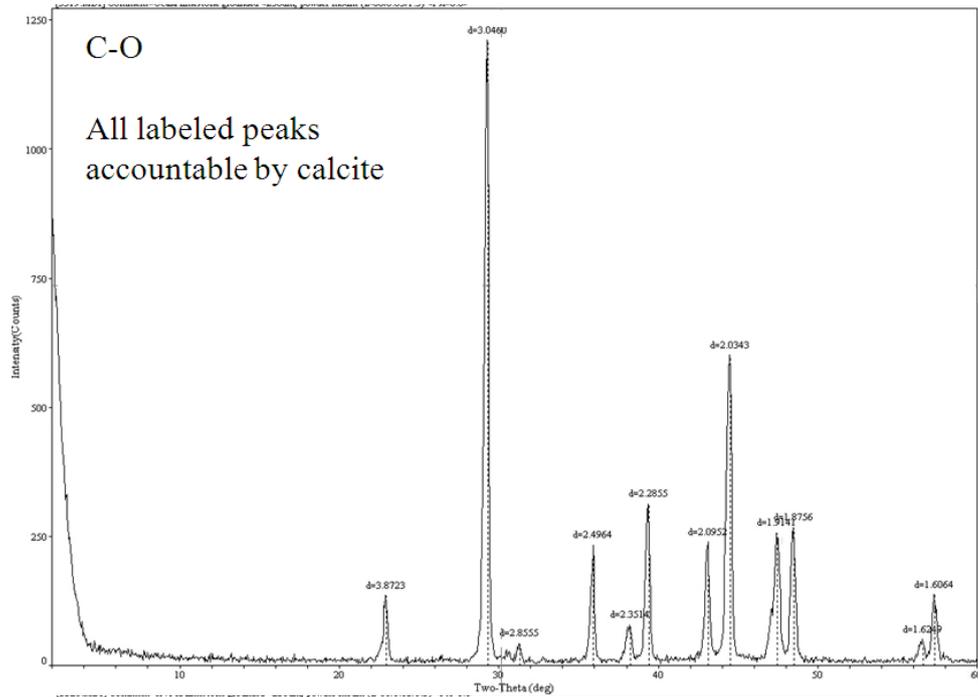


Figure D-1. Continued

APPENDIX E
HPLC PEAK RETENTION TIME OF SORBENT INDIGENOUS ORGANIC MATTER

Table E-1. HPLC peak retention time of sorbent indigenous organic matter

Sorbent name	Peak 1	Peak 2	Peak 3	Peak 4
R-O	-	11.8	12.8	-
R-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

APPENDIX F
EEM GRAPHS FOR NDOM-SORBENT PAIRS

EEM data for each NDOM-sorbent pair are presented in the form of a table consisted of three main columns: 'before adsorption' (left column), 'after adsorption' (middle), and 'EEM intensity change' (right). The EEM intensity change was generated by deducting the intensity of 'before adsorption' from that of 'after adsorption'. Therefore, change in intensity greater than zero shows desorption occurred, while less than zero means adsorption occurred. All the EEM graphs have the same scales: the horizontal axis of the EEM graph represents the emission wavelength, ranges from 200 to 700 nm, measured at 3 nm intervals, and the vertical axis represents the excitation wavelength, ranges from 200 to 450 nm, measured at 10 nm intervals. The water used in controls as background solution was deionized, photo-oxidized OC-free water.

Table F-1. EEM graphs for NDOM-sorbent pairs

Sorbent	Sorbate	Before adsorption	After adsorption	EEM intensity change
70	C-S <0.15 mm	Stream NDOM C=24.53 mg C/L		
	C-S <0.15 mm	Soil NDOM C=11.19 mg C/L		
	C-H <0.15 mm	Stream NDOM C=24.53 mg C/L		

Table F-1. Continued

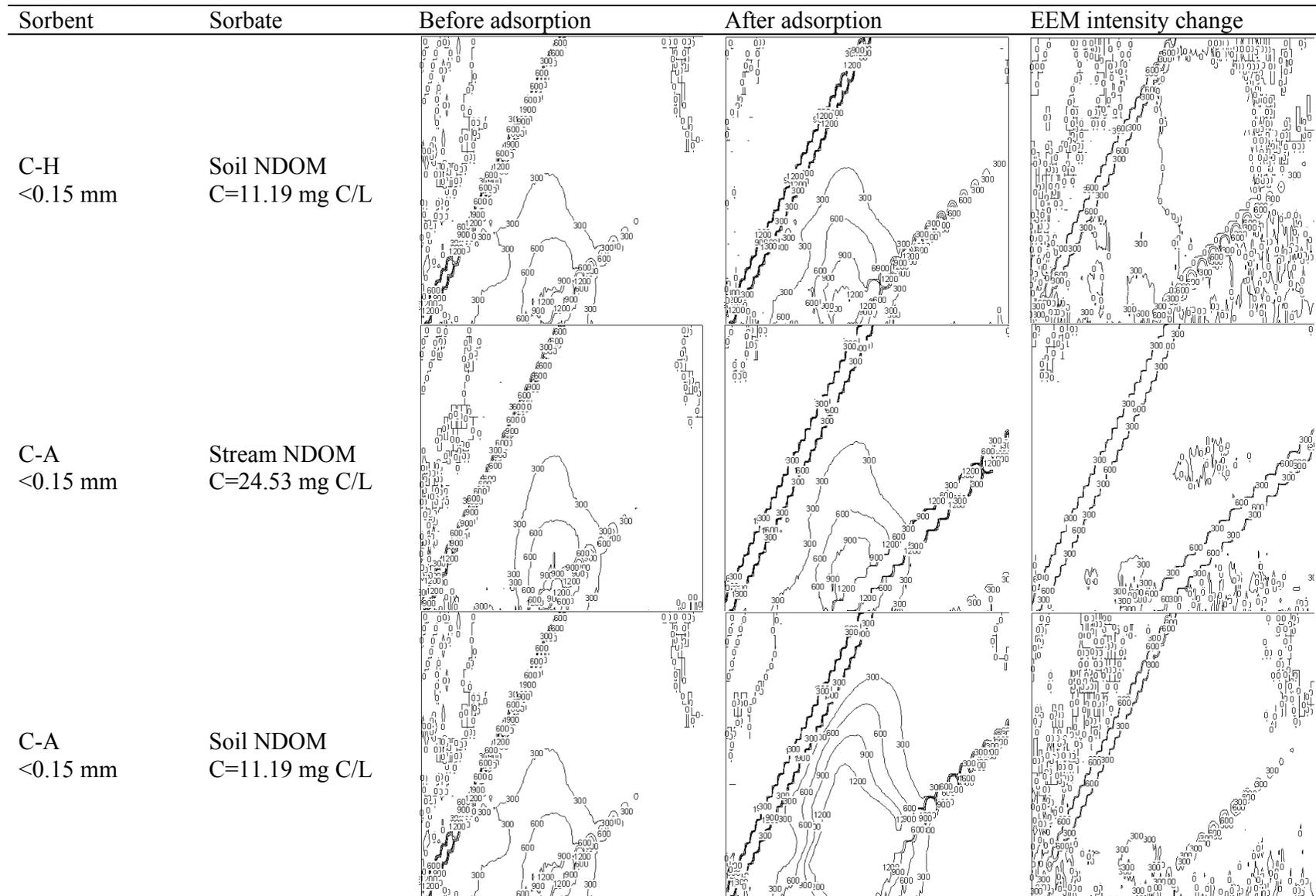


Table F-1. Continued

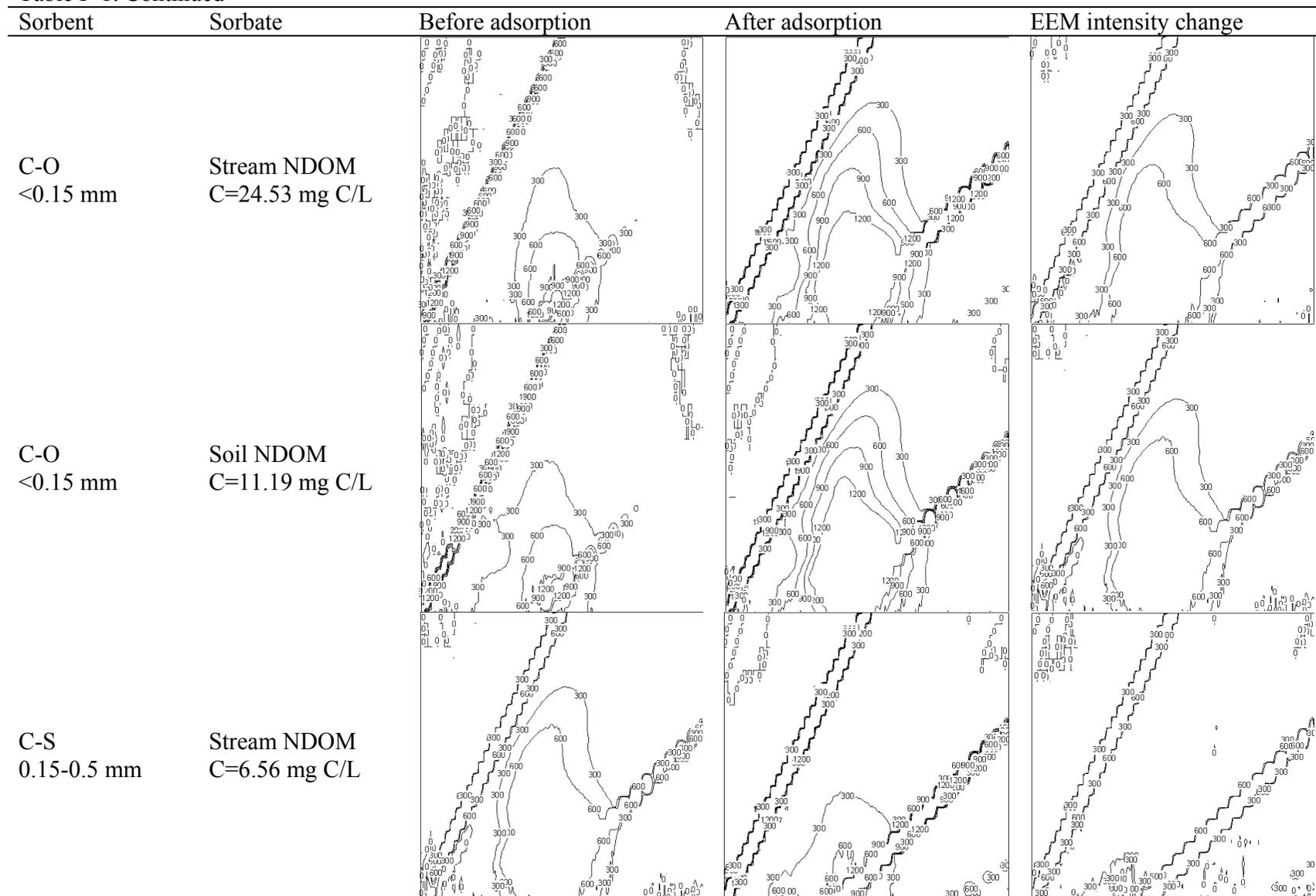


Table F-1. Continued

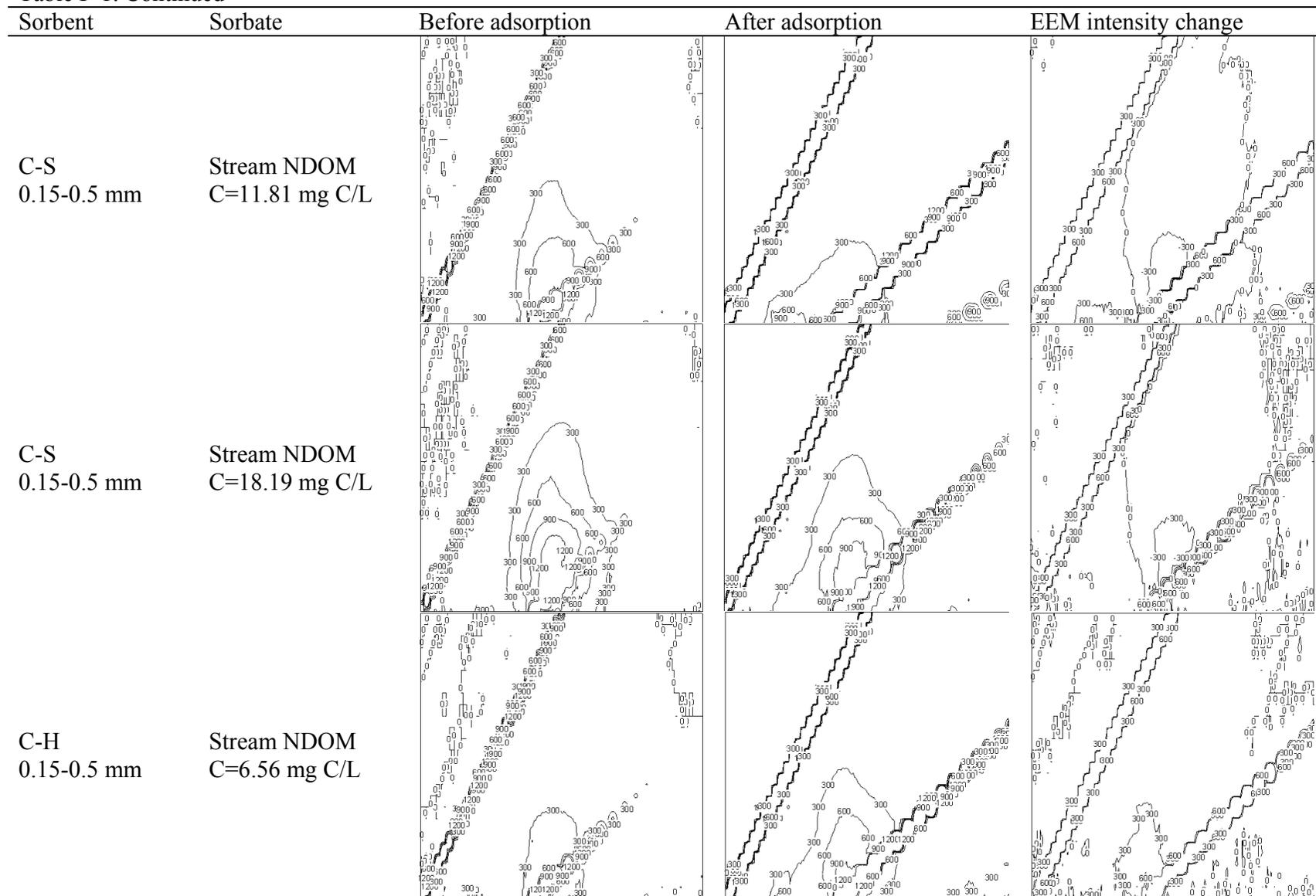


Table F-1. Continued

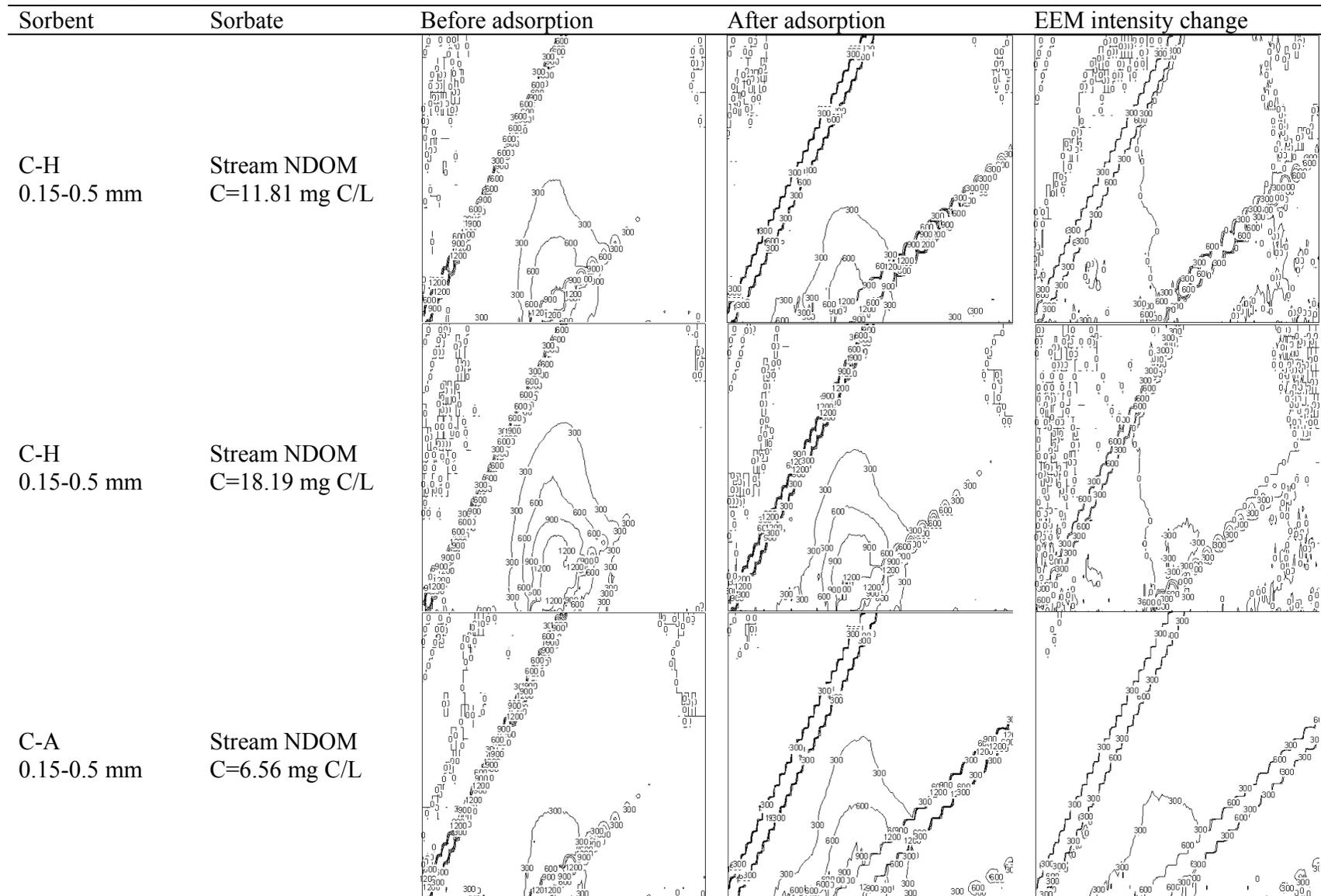


Table F-1. Continued

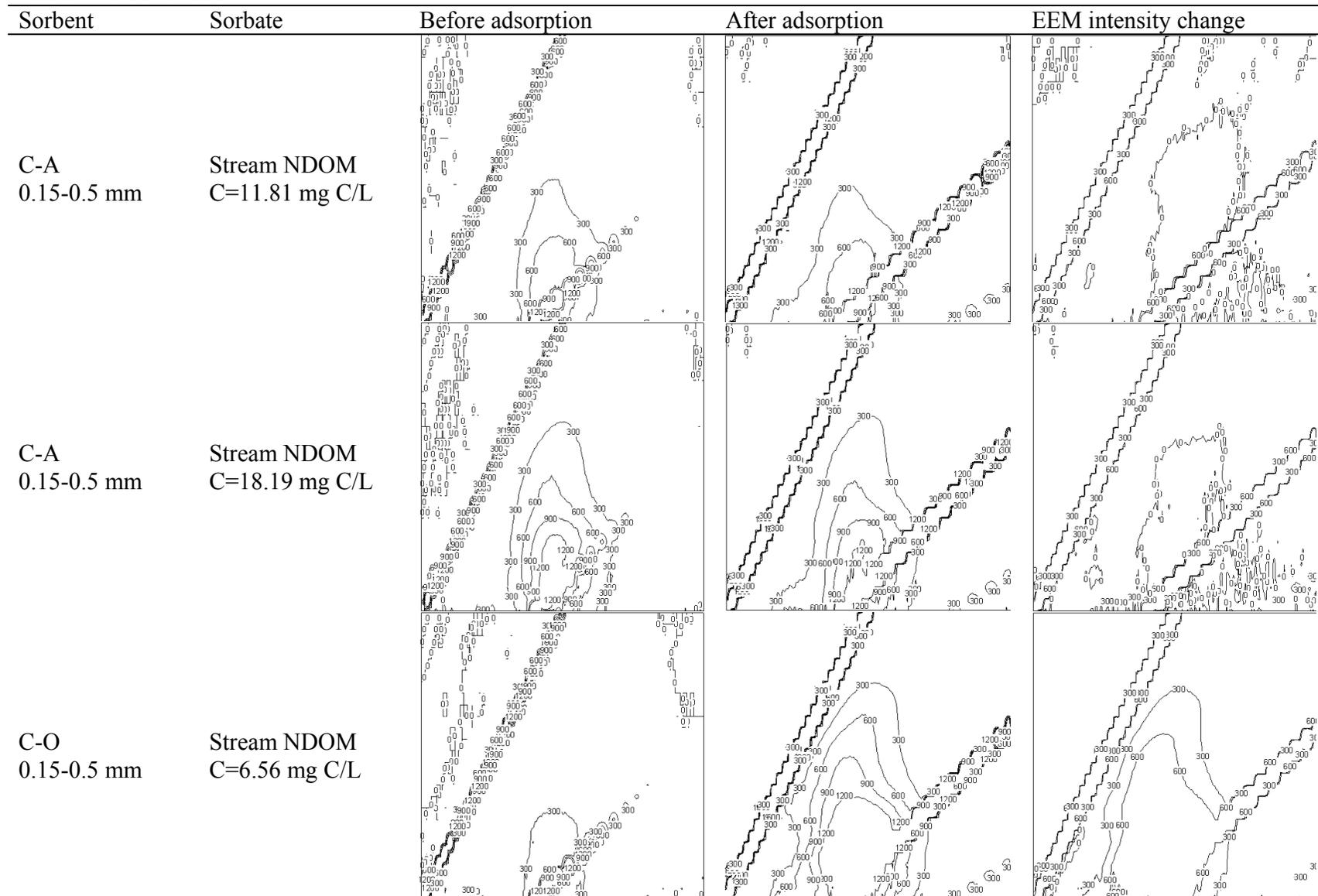


Table F-1. Continued

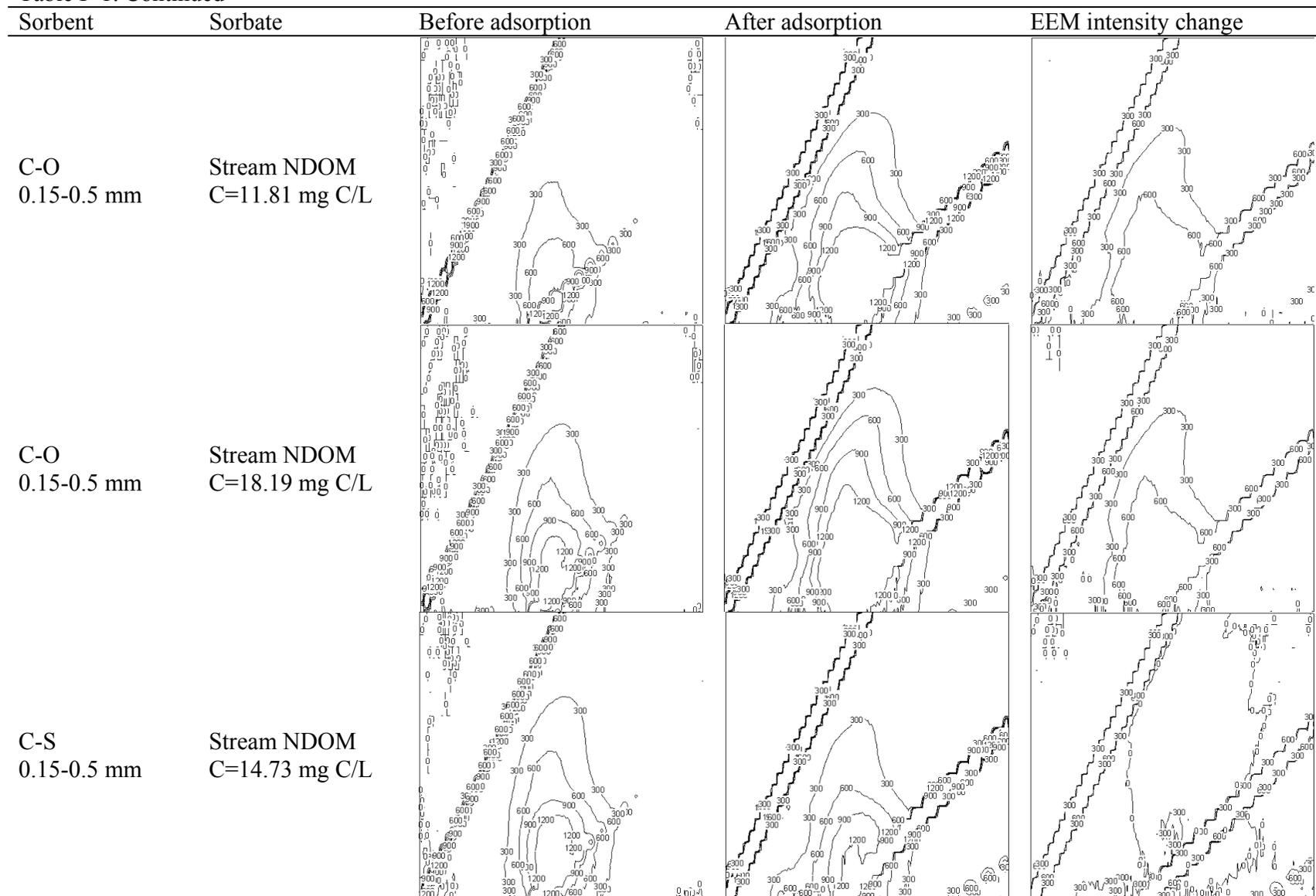


Table F-1. Continued

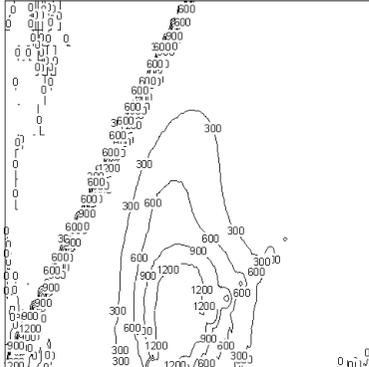
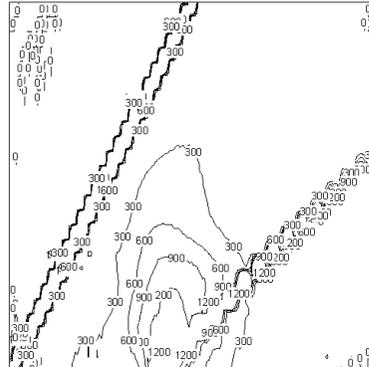
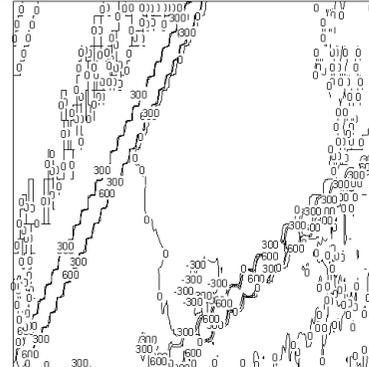
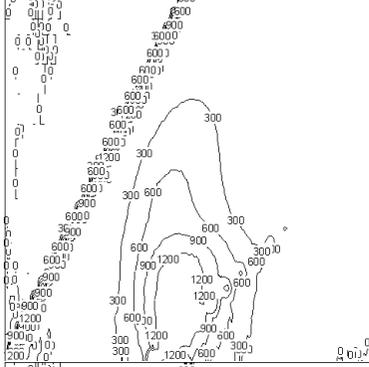
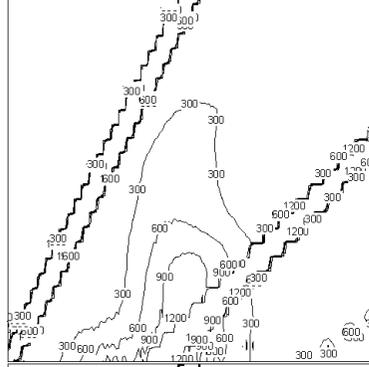
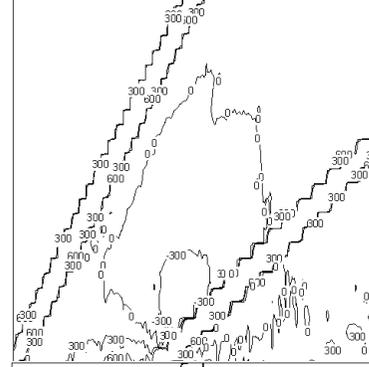
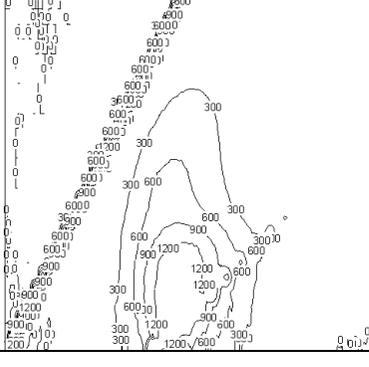
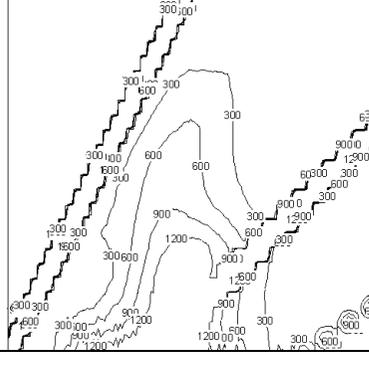
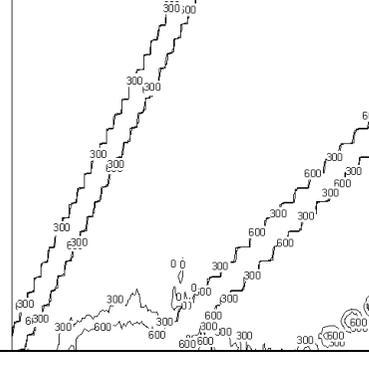
Sorbent	Sorbate	Before adsorption	After adsorption	EEM intensity change
C-H 0.15-0.5 mm	Stream NDOM C=14.73 mg C/L			
C-A 0.15-0.5 mm	Stream NDOM C=14.73 mg C/L			
C-O 0.15-0.5 mm	Stream NDOM C=14.73 mg C/L			

Table F-1. Continued

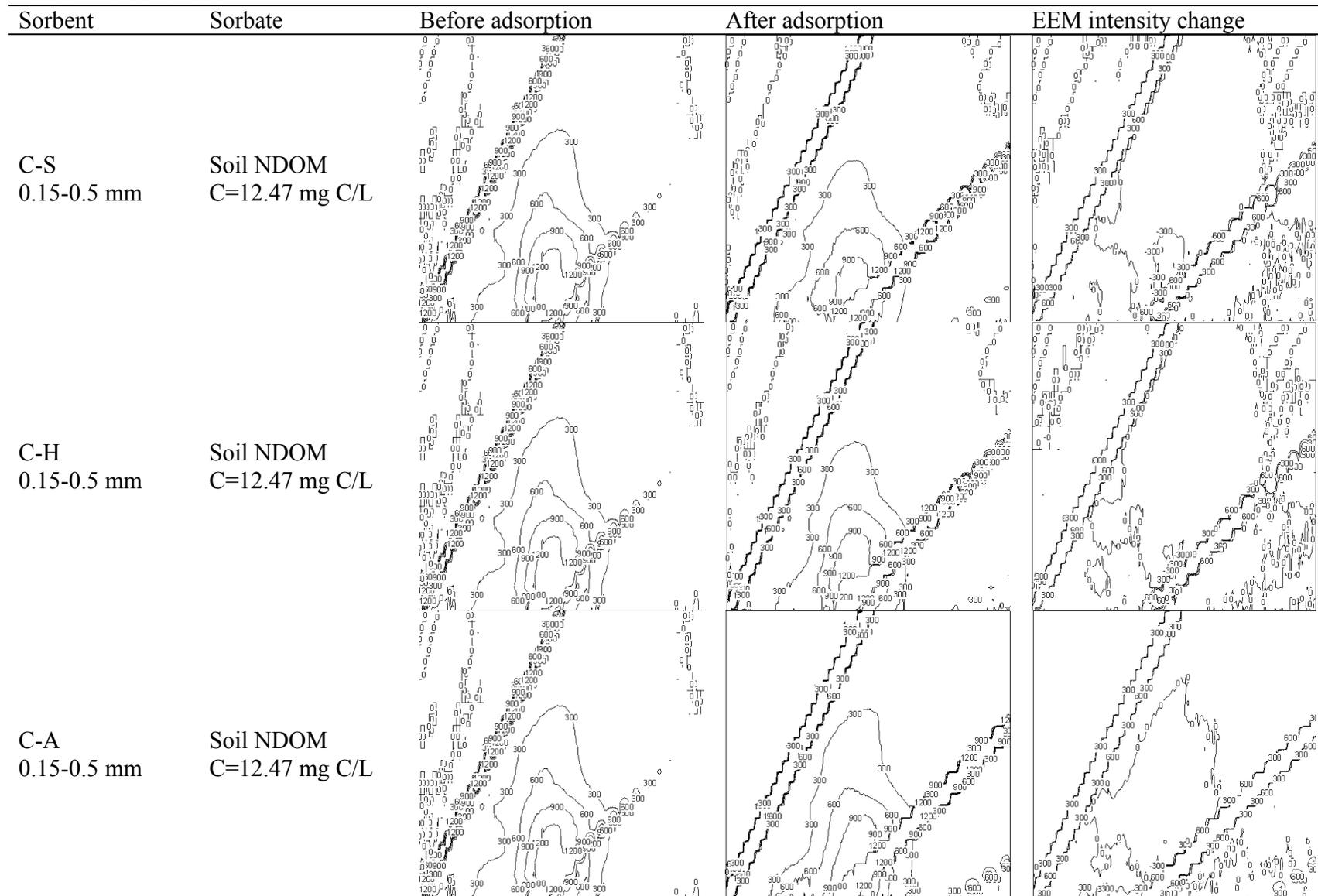
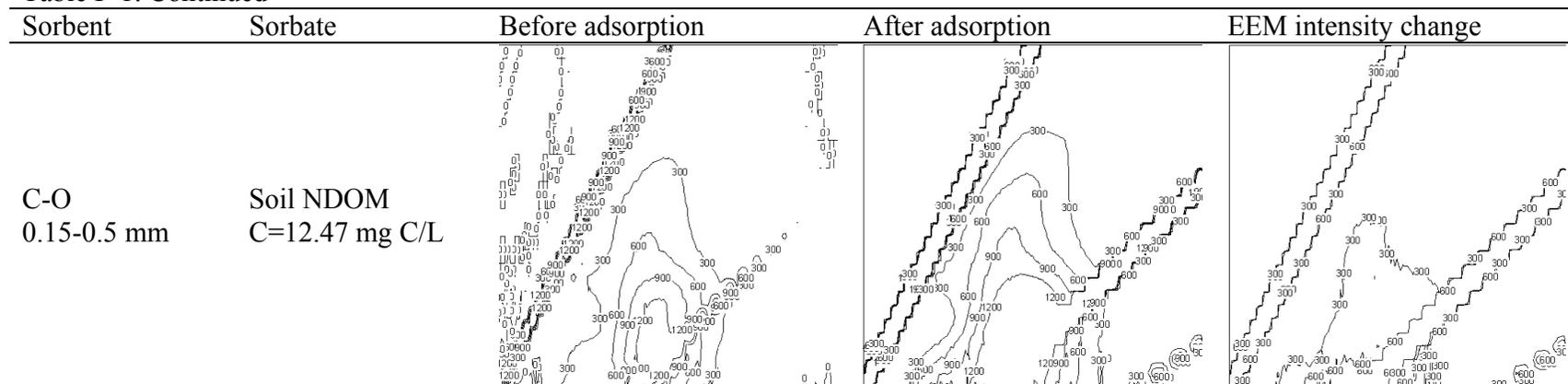


Table F-1. Continued



LIST OF REFERENCES

- Aiken, G., (2002) Organic matter in ground water. In: *U.S. Geological Survey Artificial Recharge Workshop Proceedings, Open-File Report 02-89*. U.S. Geological Survey, Sacramento, California.
- Amiri, F., Bornick, H., Worch, E., (2005) Sorption of phenols onto sandy aquifer material: the effect of dissolved organic matter (DOM). *Water Research*, 39(5), 933-941.
- Amiri, F., Rahman, M.M., Bornick, H., Worch, E., (2004) Sorption behaviour of phenols on natural sandy aquifer material during flow-through column experiments: The effect of pH. *Acta Hydrochimica Et Hydrobiologica*, 32(3), 214-224.
- Arthur, J.D., Dabous, A. A., Cowart, J. B., (2002) Mobilization of arsenic and other trace elements during aquifer storage and recovery, southwest Florida. In: *U.S. Geological Survey Artificial Recharge Workshop Proceedings, Open-File Report 02-89*. U.S. Geological Survey, Sacramento, California.
- Avena, M.J., Koopal, L.K., (1999) Kinetics of humic acid adsorption at solid-water interfaces. *Environmental Science & Technology*, 33(16), 2739-2744.
- Baham, J., Sposito, G., (1994) Adsorption of Dissolved Organic-Carbon Extracted From Sewage-Sludge on Montmorillonite and Kaolinite in the Presence of Metal-Ions. *Journal of Environmental Quality*, 23(1), 147-153.
- Baker, A., (2005) Thermal fluorescence quenching properties of dissolved organic matter. *Water Research*, 39(18), 4405-4412.
- Baker, A., Lamont-Black, J., (2001) Fluorescence of dissolved organic matter as a natural tracer of ground water. *Ground Water*, 39(5), 745-750.
- Balcke, G.U., Kulikova, N.A., Hesse, S., Kopinke, F.D., Perminova, I.V., Frimmel, F.H., (2002) Adsorption of humic substances onto kaolin clay related to their structural features. *Soil Science Society of America Journal*, 66(6), 1805-1812.
- Ball, W.P., Roberts, P.V., (1991a) Long-term Sorption of Halogenated Organic-Chemicals by Aquifer Material. 1. Equilibrium. *Environmental Science & Technology*, 25(7), 1223-1237.
- Ball, W.P., Roberts, P.V., (1991b) Long-term sorption of halogenated organic-chemicals by aquifer material. 2. intraparticle diffusion. *Environmental Science & Technology*, 25(7), 1237-1249.
- Barber, L.B., Thurman, E.M., Runnells, D.D., (1992) Geochemical Heterogeneity in a sand and gravel aquifer - effect of sediment mineralogy and particle-size on

- the sorption of chlorobenzenes. *Journal of Contaminant Hydrology*, 9(1-2), 35-54.
- Barriuso, E., Baer, U., Calvet, R., (1992) Organic-chemicals in the environment - dissolved organic-matter and adsorption-desorption of dimefuron, atrazine, and carbetamide by soils. *Journal of Environmental Quality*, 21(3), 359-367.
- Bob, M., Walker, H.W., (2001) Enhanced adsorption of natural organic matter on calcium carbonate particles through surface charge modification, pp. 17-25.
- Boyes, S., Elliott, M., (2006) Organic matter and nutrient inputs to the Humber Estuary, England. *Marine Pollution Bulletin*, 53(1-4), 136-143.
- Carmichael, L.M., Christman, R.F., Pfaender, F.K., (1997) Desorption and mineralization kinetics of phenanthrene and chrysene in contaminated soils. *Environmental Science & Technology*, 31(1), 126-132.
- Carter, P.W., (1978) Adsorption of Amino Acid-Containing Organic-Matter by Calcite and Quartz. *Geochimica Et Cosmochimica Acta*, 42(8), 1239-1242.
- Carter, P.W., Mitterer, R.M., (1978) Amino-Acid Composition of Organic-Matter Associated with Carbonate and Non-Carbonate Sediments. *Geochimica Et Cosmochimica Acta*, 42(8), 1231-1238.
- Cha, W., Choi, H., Kim, J., Kim, I.S., (2004) Evaluation of wastewater effluents for soil aquifer treatment in South Korea. *Water Science and Technology*, 50(2), 315-322.
- Chapelle, F.H., (2000) The significance of microbial processes in hydrogeology and geochemistry. *Hydrogeology Journal*, 8(1), 41-46.
- Chen, B.L., Johnson, E.J., Chefetz, B., Zhu, L.Z., Xing, B.S., (2005) Sorption of polar and nonpolar aromatic organic contaminants by plant cuticular materials: Role of polarity and accessibility. *Environmental Science & Technology*, 39(16), 6138-6146.
- Chen, B.L., Xing, B.S., (2005) Sorption and conformational characteristics of reconstituted plant cuticular waxes on montmorillonite. *Environmental Science & Technology*, 39(21), 8315-8323.
- Chi, F.H., Amy, G.L., (2004) Kinetic study on the sorption of dissolved natural organic matter onto different aquifer materials: the effects of hydrophobicity and functional groups. *Journal of Colloid and Interface Science*, 274(2), 380-391.

- Chin, Y.P., Aiken, G., Oloughlin, E., (1994) Molecular-Weight, Polydispersity, and Spectroscopic Properties of Aquatic Humic Substances. *Environmental Science & Technology*, 28(11), 1853-1858.
- Coble, P.G., (1996) Characterization of marine and terrestrial DOM in seawater using excitation emission matrix spectroscopy. *Marine Chemistry*, 51(4), 325-346.
- Curtis, G.P., Roberts, P.V., Reinhard, M., (1986) A natural gradient experiment on solute transport in a sand aquifer. 4. sorption of organic solutes and its influence on mobility. *Water Resources Research*, 22(13), 2059-2067.
- Davis, J.A., (1982) Adsorption of Natural Dissolved Organic-Matter at the Oxide Water Interface. *Geochimica Et Cosmochimica Acta*, 46(11), 2381-2393.
- Day, G.M., Hart, B.T., McKelvie, I.D., Beckett, R., (1994) Adsorption of Natural Organic-Matter Onto Goethite. *Colloids and Surfaces a-Physicochemical and Engineering Aspects*, 89(1), 1-13.
- de Leeuw, N.H., (2004) A computer modelling study of the uptake and segregation of fluoride ions at the hydrated hydroxyapatite (0001) surface: introducing Ca-10(PO₄)₆(OH)₂ potential model, pp. 1860-1866.
- Ditoro, D.M., Horzempa, L.M., (1982) Reversible and resistant component of PCB adsorption desorption - isotherms. *Environmental Science & Technology*, 16(9), 594-602.
- Drever, J.I., (2002a) The Geochemistry of Natural Waters: Surface and Groundwater Environments, pp. 114-116. Prentice Hall, Upper Saddle River, NJ.
- Drever, J.I., (2002b) The Geochemistry of Natural Waters: Surface and Groundwater Environments, pp. 88-90. Prentice Hall, Upper Saddle River, NJ.
- Drever, J.I., (2002c) The Geochemistry of Natural Waters: Surface and Groundwater Environments, pp. 419-442. Prentice Hall, Upper Saddle River, NJ.
- Drewes, J.E., Quanrud, D.M., Amy, G.L., Westerhoff, P.K., (2006) Character of organic matter in soil-aquifer treatment systems. *Journal of Environmental Engineering-Asce*, 132(11), 1447-1458.
- Dunnivant, F.M., Schwarzenbach, R.P., Macalady, D.L., (1992) Reduction of Substituted Nitrobenzenes in Aqueous-Solutions Containing Natural Organic-Matter. *Environmental Science & Technology*, 26(11), 2133-2141.
- Ehrlich, H.L., (1998) Geomicrobiology: its significance for geology. *Earth-Science Reviews*, 45(1-2), 45-60.

- Essington, M.E., (2004a) Soil and Water Chemistry: An Integrative Approach, pp. 163-167. CRC Press, Boca Raton.
- Essington, M.E., (2004b) Soil and Water Chemistry: An Integrative Approach, pp. 338-339. CRC Press, Boca Raton.
- Essington, M.E., (2004c) Soil and Water Chemistry: An Integrative Approach, pp. 358-364. CRC Press, Boca Raton.
- Essington, M.E., (2004d) Soil and Water Chemistry: An Integrative Approach, pp. 335. CRC Press, Boca Raton.
- Findlay, S.E.G., Sinsabaugh, R.L., Sobczak, W.V., Hoostal, M., (2003) Metabolic and structural response of hyporheic microbial communities to variations in supply of dissolved organic matter. *Limnology and Oceanography*, 48(4), 1608-1617.
- Fisher, T.R., Hagy, J.D., Boynton, W.R., Williams, M.R., (2006) Cultural eutrophication in the Choptank and Patuxent estuaries of Chesapeake Bay. *Limnology and Oceanography*, 51(1), 435-447.
- Fredd, C.N., Fogler, H.S., (1998) The influence of chelating agents on the kinetics of calcite dissolution. *Journal of Colloid and Interface Science*, 204(1), 187-197.
- Frimmel, F.H., (1998) Characterization of natural organic matter as major constituents in aquatic systems. *Journal of Contaminant Hydrology*, 35(1-3), 201-216.
- Frye, G.C., Thomas, M.M., (1993) Adsorption of Organic-Compounds on Carbonate Minerals .2. Extraction of Carboxylic-Acids from Recent and Ancient Carbonates. *Chemical Geology*, 109(1-4), 215-226.
- Geffroy, C., Stuart, M.A.C., Wong, K., Cabane, B., Bergeron, V., (2000) Adsorption of nonionic surfactants onto polystyrene: Kinetics and reversibility. *Langmuir*, 16(16), 6422-6430.
- Grathwohl, P., Reinhard, M., (1993) Desorption of trichloroethylene in aquifer material - rate limitation at the grain scale. *Environmental Science & Technology*, 27(12), 2360-2366.
- Gu, B.H., Schmitt, J., Chen, Z., Liang, L.Y., McCarthy, J.F., (1995) Adsorption and Desorption of Different Organic-Matter Fractions on Iron-Oxide. *Geochimica Et Cosmochimica Acta*, 59(2), 219-229.
- Gu, B.H., Schmitt, J., Chen, Z.H., Liang, L.Y., McCarthy, J.F., (1994) Adsorption and Desorption of Natural Organic-Matter on Iron-Oxide - Mechanisms and Models. *Environmental Science & Technology*, 28(1), 38-46.

- Hancock, P.J., Boulton, A.J., Humphreys, W.F., (2005) Aquifers and hyporheic zones: Towards an ecological understanding of groundwater. *Hydrogeology Journal*, 13(1), 98-111.
- Hedges, J.I., Oades, J.M., (1997) Comparative organic geochemistries of soils and marine sediments. *Organic Geochemistry*, 27(7-8), 319-361.
- Hendry, M.J., Wassenaar, L.I., (2005) Origin and migration of dissolved organic carbon fractions in a clay-rich aquitard: C-14 and delta C-13 evidence. *Water Resources Research*, 41(2).
- Her, N., Amy, G., McKnight, D., Sohn, J., Yoon, Y.M., (2003) Characterization of DOM as a function of MW by fluorescence EEM and HPLC-SEC using UVA, DOC, and fluorescence detection. *Water Research*, 37(17), 4295-4303.
- Hoch, A.R., Reddy, M.M., Aiken, G.R., (2000) Calcite crystal growth inhibition by humic substances with emphasis on hydrophobic acids from the Florida Everglades. *Geochimica Et Cosmochimica Acta*, 64(1), 61-72.
- Hur, J., Schlautman, M.A., (2003) Molecular weight fractionation of humic substances by adsorption onto minerals. *Journal of Colloid and Interface Science*, 264(2), 313-321.
- Inskeep, W.P., Bloom, P.R., (1986) Kinetics of Calcite Precipitation in the Presence of Water-Soluble Organic-Ligands. *Soil Science Society of America Journal*, 50(5), 1167-1172.
- Jardine, P.M., Weber, N.L., McCarthy, J.F., (1989) Mechanisms of Dissolved Organic-Carbon Adsorption on Soil. *Soil Science Society of America Journal*, 53(5), 1378-1385.
- Johnson, S.B., Yoon, T.H., Kocar, B.D., Brown, G.E., (2004) Adsorption of organic matter at mineral/water interfaces. 2. Outer-sphere adsorption of maleate and implications for dissolution processes. *Langmuir*, 20(12), 4996-5006.
- Kahle, M., Kleber, M., Jahn, R., (2003) Retention of dissolved organic matter by illitic soils and clay fractions: Influence of mineral phase properties. *Journal of Plant Nutrition and Soil Science-Zeitschrift Fur Pflanzenernahrung Und Bodenkunde*, 166(6), 737-741.
- Kahle, M., Kleber, M., Jahn, R., (2004) Retention of dissolved organic matter by phyllosilicate and soil clay fractions in relation to mineral properties, pp. 269-276.
- Kaiser, K., (2003) Sorption of natural organic matter fractions to goethite (alpha-FeOOH): effect of chemical composition as revealed by liquid-state C-13 NMR and wet-chemical analysis. *Organic Geochemistry*, 34(11), 1569-1579.

- Kaiser, K., Guggenberger, G., (2003) Mineral surfaces and soil organic matter. *European Journal of Soil Science*, 54(2), 219-236.
- Karapanagioti, H.K., Gossard, C.M., Strevett, K.A., Kolar, R.L., Sabatini, D.A., (2001) Model coupling intraparticle diffusion/sorption, nonlinear sorption, and biodegradation processes. *Journal of Contaminant Hydrology*, 48(1-2), 1-21.
- Kleineidam, S., Rugner, H., Grathwohl, P., (2004) Desorption kinetics of phenanthrene in aquifer material lacks hysteresis. *Environmental Science & Technology*, 38(15), 4169-4175.
- Lau, L.S., Mink, J.F., (1987) Organic Contamination of Groundwater - a Learning-Experience. *Journal American Water Works Association*, 79(8), 37-42.
- Lee, Y.J., Elzinga, E.J., Reeder, R.J., (2005) Cu(II) adsorption at the calcite-water interface in the presence of natural organic matter: kinetic studies and molecular-scale characterization. *Geochimica Et Cosmochimica Acta*, 69(1), 49-61.
- Leenheer, J.A., (2002) Processes Controlling Attenuation of Dissolved Organic Matter in the Subsurface. In: *U.S. Geological Survey Artificial Recharge Workshop Proceedings, Open-File Report 02-89* (Ed. by G.R.A.a.E.L. Kuniandy). U.S. Geological Survey, Sacramento, California.
- Lepane, V., (2001) Characterization of Baltic Sea dissolved organic matter as oil shale precursor by separation and fractionation by adsorption chromatographic XAD method, and size exclusion chromatography. *Oil Shale*, 18(3), 239-257.
- Lepane, V., Kudrjashova, M., (2001) High-performance size exclusion chromatographic characterization of humic substances and dissolved organic matter from Baltic aquatic environment. *Oil Shale*, 18(4), 350-372.
- Liang, L.Y., McCarthy, J.F., Jolley, L.W., McNabb, J.A., Mehlhorn, T.L., (1993) Iron Dynamics - Transformation of Fe (II)/Fe (III) During Injection of Natural Organic-Matter in a Sandy Aquifer. *Geochimica Et Cosmochimica Acta*, 57(9), 1987-1999.
- Lin, Y.P., Singer, P.C., (2005) Inhibition of calcite crystal growth by polyphosphates. *Water Research*, 39(19), 4835-4843.
- Lin, Y.P., Singer, P.C., Aiken, G.R., (2004) Inhibition of heterogeneous calcite crystallization by Suwannee River fulvic acid: Kinetics, mechanism and thermodynamics. *Abstracts of Papers of the American Chemical Society*, 228, U611-U611.

- Lindroos, A.J., Kitunen, V., Derome, J., Helmisaari, H.S., (2002) Changes in dissolved organic carbon during artificial recharge of groundwater in a forested esker in Southern Finland. *Water Research*, 36(20), 4951-4958.
- Lovley, D.R., Chapelle, F.H., (1995) Deep subsurface microbial processes. *Reviews of Geophysics*, 33(3), 365-381.
- Lu, Y.Q., Miller, J.D., (2002) Carboxyl stretching vibrations of spontaneously adsorbed and LB-transferred calcium carboxylates as determined by FTIR internal reflection spectroscopy. *Journal of Colloid and Interface Science*, 256(1), 41-52.
- Luttge, A., Conrad, P.G., (2004) Direct observation of microbial inhibition of calcite dissolution. *Applied and Environmental Microbiology*, 70(3), 1627-1632.
- Mazzullo, S.J., Harris, P.M., (1992) Mesogenetic Dissolution - Its Role in Porosity Development in Carbonate Reservoirs. *Aapg Bulletin-American Association of Petroleum Geologists*, 76(5), 607-620.
- McCarthy, J.F., Williams, T.M., Liang, L.Y., Jardine, P.M., Jolley, L.W., Taylor, D.L., Palumbo, A.V., Cooper, L.W., (1993) Mobility of Natural Organic-Matter in a Sandy Aquifer. *Environmental Science & Technology*, 27(4), 667-676.
- McCarthy, J.F., Zachara, J.M., (1989) Subsurface Transport of Contaminants - Mobile Colloids in the Subsurface Environment may Alter the Transport of Contaminants. *Environmental Science & Technology*, 23(5), 496-502.
- McKnight, D.M., Bencala, K.E., Zellweger, G.W., Aiken, G.R., Feder, G.L., Thorn, K.A., (1992) Sorption of Dissolved Organic-Carbon by Hydrous Aluminum and Iron-Oxides Occurring at the Confluence of Deer Creek With the Snake River, Summit County, Colorado. *Environmental Science & Technology*, 26(7), 1388-1396.
- McMahon, P.B., Vroblesky, D.A., Bradley, P.M., Chapelle, F.H., Gullett, C.D., (1995) Evidence for Enhanced Mineral Dissolution in Organic Acid-Rich Shallow Ground-Water. *Ground Water*, 33(2), 207-216.
- Meier, M., Chin, Y.P., Maurice, P., (2004) Variations in the composition and adsorption behavior of dissolved organic matter at a small, forested watershed. *Biogeochemistry*, 67(1), 39-56.
- Meier, M., Namjesnik-Dejanovic, K., Maurice, P.A., Chin, Y.P., Aiken, G.R., (1999) Fractionation of aquatic natural organic matter upon sorption to goethite and kaolinite. *Chemical Geology*, 157(3-4), 275-284.

- Muller, P.J., Suess, E., Ungerer, C.A., (1986) Amino-Acids and Amino-Sugars of Surface Particulate and Sediment Trap Material from Waters of the Scotia Sea. *Deep-Sea Research Part a-Oceanographic Research Papers*, 33(6), 819-838.
- Murphy, E.M., Schramke, J.A., (1998) Estimation of microbial respiration rates in groundwater by geochemical modeling constrained with stable isotopes. *Geochimica Et Cosmochimica Acta*, 62(21-22), 3395-3406.
- Murphy, E.M., Schramke, J.A., Fredrickson, J.K., Bledsoe, H.W., Francis, A.J., Sklarew, D.S., Linehan, J.C., (1992) The Influence of Microbial Activity and Sedimentary Organic-Carbon on the Isotope Geochemistry of the Middendorf Aquifer. *Water Resources Research*, 28(3), 723-740.
- Murphy, E.M., Zachara, J.M., Smith, S.C., (1990) Influence of Mineral Bound Humic Acids on the Sorption of Hydrophobic Organic-Compounds. *Abstracts of Papers of the American Chemical Society*, 199, 98-ENVR.
- Namjesnik-Dejanovic, K., Maurice, P.A., Aiken, G.R., Cabaniss, S., Chin, Y.P., Pullin, M.J., (2000) Adsorption and fractionation of a muck fulvic acid on kaolinite and goethite at pH 3.7, 6, and 8. *Soil Science*, 165(7), 545-559.
- Ochs, M., Cosovic, B., Stumm, W., (1994) Coordinative and Hydrophobic Interaction of Humic Substances With Hydrophilic Al₂O₃ and Hydrophobic Mercury Surfaces. *Geochimica Et Cosmochimica Acta*, 58(2), 639-650.
- Parlanti, E., Worz, K., Geoffroy, L., Lamotte, M., (2000) Dissolved organic matter fluorescence spectroscopy as a tool to estimate biological activity in a coastal zone submitted to anthropogenic inputs. *Organic Geochemistry*, 31(12), 1765-1781.
- Pavelic, P., Nicholson, B.C., Dillon, P.J., Barry, K.E., (2005) Fate of disinfection by-products in groundwater during aquifer storage and recovery with reclaimed water. *Journal of Contaminant Hydrology*, 77(1-2), 119-141.
- Perry, T.D., Duckworth, O.W., McNamara, C.J., Martin, S.T., Mitchell, R., (2003) Accelerated calcite dissolution caused by alginic acid. *Abstracts of Papers of the American Chemical Society*, 226, U591-U591.
- Perry, T.D., Duckworth, O.W., McNamara, C.J., Martin, S.T., Mitchell, R., (2004) Effects of the biologically produced polymer alginic acid on macroscopic and microscopic calcite dissolution rates. *Environmental Science & Technology*, 38(11), 3040-3046.
- Petrovic, M., Kastelan-Macan, M., Horvat, A.J.M., (1999) Interactive sorption of metal ions and humic acids onto mineral particles. *Water Air and Soil Pollution*, 111(1-4), 41-56.

- Phillips, B.L., Lee, Y.J., Reeder, R.J., (2005) Organic coprecipitates with calcite: NMR spectroscopic evidence. *Environmental Science & Technology*, 39(12), 4533-4539.
- Pignatello, J.J., Ferrandino, F.J., Huang, L.Q., (1993) Elution of aged and freshly added herbicides from a soil. *Environmental Science & Technology*, 27(8), 1563-1571.
- Plank, J., Bassioni, G., (2007) Adsorption of carboxylate anions on a CaCO₃ surface. *Zeitschrift Fur Naturforschung Section B-a Journal of Chemical Sciences*, 62(10), 1277-1284.
- Price, R.E., Pichler, T., (2006) Abundance and mineralogical association of arsenic in the Suwannee Limestone (Florida): Implications for arsenic release during water-rock interaction, pp. 44-56.
- Pu, X.C., Cutright, T.J., (2006) Sorption-desorption behavior of PCP on soil organic matter and clay minerals. *Chemosphere*, 64(6), 972-983.
- Raber, B., Kogel-Knabner, I., Stein, C., Klem, D., (1998) Partitioning of polycyclic aromatic hydrocarbons to dissolved organic matter from different soils. *Chemosphere*, 36(1), 79-97.
- Ran, Y., Xing, B.S., Rao, P.S.C., Fu, J.M., (2004) Importance of adsorption (hole-filling) mechanism for hydrophobic organic contaminants on an aquifer kerogen isolate. *Environmental Science & Technology*, 38(16), 4340-4348.
- Randazzo, A.F., Jones, D.S., (1997) *The Geology of Florida*. University Press of Florida.
- Rauch, T., Drewes, J.E., (2005) Quantifying biological organic carbon removal in groundwater recharge systems. *Journal of Environmental Engineering-Asce*, 131(6), 909-923.
- Rauch, T., Drewes, L., (2004) Assessing the removal potential of soil-aquifer treatment systems for bulk organic matter. *Water Science and Technology*, 50(2), 245-253.
- Roberts, P.V., Goltz, M.N., Mackay, D.M., (1986) A natural gradient experiment on solute transport in a sand aquifer. 3. retardation estimates and mass balances for organic solutes. *Water Resources Research*, 22(13), 2047-2058.
- Ross, N., Villemur, R., Deschenes, L., Samson, R., (2001) Clogging of a limestone fracture by stimulating groundwater microbes. *Water Research*, 35(8), 2029-2037.

- Rugner, H., Kleineidam, S., Grathwohl, P., (1999) Long term sorption kinetics of phenanthrene in aquifer materials. *Environmental Science & Technology*, 33(10), 1645-1651.
- Saito, T., Koopal, L.K., van Riemsdijk, W.H., Nagasaki, S., Tanaka, S., (2004) Adsorption of humic acid on goethite: Isotherms, charge adjustments, and potential profiles. *Langmuir*, 20(3), 689-700.
- Schlautman, M.A., Morgan, J.J., (1994) Adsorption of Aquatic Humic Substances on Colloidal-Size Aluminum-Oxide Particles - Influence of Solution Chemistry. *Geochimica Et Cosmochimica Acta*, 58(20), 4293-4303.
- Schwarzenbach, R.P., Gschwend, P.M., Imboden, D.M., (2003a) Environmental Organic Chemistry (Second Edition). In: S. Edition (Ed.) (Ed. by S. Edition), pp. 280-283. Wiley-Interscience.
- Schwarzenbach, R.P., Gschwend, P.M., Imboden, D.M., (2003b) Environmental Organic Chemistry (Second Edition). In: S. Edition (Ed.) (Ed. by S. Edition), pp. 291. Wiley-Interscience.
- Selim, H.M., Buchter, B., Hinz, C., Ma, L., (1992) Modeling the transport and retention of cadmium in soils - multireaction and multicomponent approaches. *Soil Science Society of America Journal*, 56(4), 1004-1015.
- Simoni, S.F., Schafer, A., Harms, H., Zehnder, A.J.B., (2001) Factors affecting mass transfer limited biodegradation in saturated porous media. *Journal of Contaminant Hydrology*, 50(1-2), 99-120.
- Specht, C.H., Kumke, M.U., Frimmel, F.H., (2000) Characterization of NOM adsorption to clay minerals by size exclusion chromatography. *Water Research*, 34(16), 4063-4069.
- Sposito, G., (1984) *The Surface Chemistry of Soils*. Oxford University Press.
- Sposito, G., (2004) *The Surface of Natural Particles*. Oxford University Press.
- Thomas, M.M., Clouse, J.A., Longo, J.M., (1993) Adsorption of organic-compounds on carbonate minerals. 3. influence on dissolution rates. *Chemical Geology*, 109(1-4), 227-237.
- Tipping, E., (1981) The Adsorption of Aquatic Humic Substances by Iron-Oxides. *Geochimica Et Cosmochimica Acta*, 45(2), 191-199.
- Tipping, E., Marker, A.F.H., Butterwick, C., Collett, G.D., Cranwell, P.A., Ingram, J.K.G., Leach, D.V., Lishman, J.P., Pinder, A.C., Rigg, E., Simon, B.M., (1997) Organic carbon in the Humber rivers. *Science of the Total Environment*, 194, 345-355.

- Tombacz, E., Libor, Z., Illes, E., Majzik, A., Klumpp, E., (2004) The role of reactive surface sites and complexation by humic acids in the interaction of clay mineral and iron oxide particles, pp. 257-267.
- Ussiri, D.A.N., Johnson, C.E., (2004) Sorption of organic carbon fractions by Spodosol mineral horizons. *Soil Science Society of America Journal*, 68(1), 253-262.
- Vaccari, D.A., Kaouris, M., (1988) A model for irreversible adsorption hysteresis. *Journal of Environmental Science and Health Part a-Environmental Science and Engineering & Toxic and Hazardous Substance Control*, 23(8), 797-822.
- Vanderzalm, J.L., La Salle, C.L.G., Dillon, P.J., (2006) Fate of organic matter during aquifer storage and recovery (ASR) of reclaimed water in a carbonate aquifer. *Applied Geochemistry*, 21(7), 1204-1215.
- Wang, K.J., Xing, B.S., (2005) Structural and sorption characteristics of adsorbed humic acid on clay minerals. *Journal of Environmental Quality*, 34(1), 342-349.
- Werth, C.J., McMillan, S.J., Castilla, H.J., (2000) Structural evaluation of slow desorbing sites in model and natural solids using temperature stepped desorption profiles. 1. Model development. *Environmental Science & Technology*, 34(14), 2959-2965.
- Wu, Y., (2003) Mechanism analysis of hazards caused by the interaction between groundwater and geo-environment. *Environmental Geology*, 44(7), 811-819.
- Wu, Y.T., Grant, C., (2002) Effect of chelation chemistry of sodium polyaspartate on the dissolution of calcite. *Langmuir*, 18(18), 6813-6820.
- Xia, G.S., Ball, W.P., (1999) Adsorption-partitioning uptake of nine low-polarity organic chemicals on a natural sorbent. *Environmental Science & Technology*, 33(2), 262-269.
- Yoon, T.H., Johnson, S.B., Brown, G.E., (2005) Adsorption of organic matter at mineral/water interfaces. IV. Adsorption of humic substances at boehmite/water interfaces and impact on boehmite dissolution. *Langmuir*, 21(11), 5002-5012.
- Zhou, Q.H., Cabaniss, S.E., Maurice, P.A., (2000) Considerations in the use of high-pressure size exclusion chromatography (HPSEC) for determining molecular weights of aquatic humic substances. *Water Research*, 34(14), 3505-3514.
- Zhou, Q.H., Maurice, P.A., Cabaniss, S.E., (2001) Size fractionation upon adsorption of fulvic acid on goethite: Equilibrium and kinetic studies. *Geochimica Et Cosmochimica Acta*, 65(5), 803-812.

BIOGRAPHICAL SKETCH

Jin Jin was born in Shanghai, China, in July 1984. He attended University of Science and Technology of China (USTC) from 2002 through 2006. Upon earning B.S. in environmental sciences from USTC, he entered University of Florida and began his graduate study in the Department of Geological Sciences under the guidance of Dr. Andrew R. Zimmerman. Jin served as both teaching and research assistant during his graduate study and received M.S. in geology in May 2009. He will continue to pursue his interests in environmental studies by enrolling in a PhD program.