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Drying effects on sorption capacity of coastal sediment: The importance of architecture and polarity of organic matter

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Abstract

Investigations on how desiccation changes sorption of organic compounds by salt marsh sediments provide insight into the physical and chemical properties of these wide-spread coastal sediments. We measured sorption of compounds with different polarities (lysine, tyrosine, naphthalene and aniline) onto natural sediments and sediments that were dried and rewetted. Sorption of lysine by marsh sediment decreased significantly when the sediment was dried using a freeze-drier, oven, or desiccator, and sorption capacity was not restored when sediments were rewetted. In contrast to lysine, the sorption capacity of more hydrophobic compounds (tyrosine, aniline and naphthalene) increased significantly after salt marsh sediment was dried. These results suggest that drying greatly increased sediment hydrophobicity. Consistently, water drop penetration time, an index of hydrophobicity, was significantly lower for combusted sediments than for those that were simply dried. Sediments treated with EDTA, or boiled in seawater, exhibited a similar or even greater reduction in lysine sorption capacity compared with sediments that were dried. Water retention capacity of salt marsh sediment decreased 50% after sediment was dried. The effects of pH and salinity on lysine sorption in wet and dry sediments suggest that carboxyl groups play a major role in lysine sorption through cation ion exchange, and drying may reduce access to carboxyl groups. We hypothesize that the three-dimensional (3D) structure of organic matter, originating mainly from *Spartina alterniflora*, is an important factor controlling sorption capacity in salt marsh sediment. The drying process makes sedimentary organic matter change conformation, shrink in volume, and expose hydrophobic groups, thus becoming more hydrophobic. In environments with wet and dry cycles, the distribution of hydrophobic or hydrophilic compounds between solution and particulate phases could thus be influenced by the 3D structure and polarity of organic matter.

1. Introduction

Soils and intertidal sediments are often subjected to wet–dry cycles. Most surface soils are wetted (hydrated) in summer and dried (dehydrated) in winter, although short term flood or drought conditions can occur at any time. Salt marsh and intertidal sediments can have daily wet–dry cycles due to the rising and falling tide. Soils and sediments consist of an inorganic fraction including sand, silt, and clay minerals, and an organic network including detritus, humic substances, sorbed organic matter and living biota. Under dry conditions, dehydration can alter the three-dimensional (3D) structure of soils and sediments; thus dried sediments may behave differently than never-dried sediments. For example, water repellency (or hydrophobicity) is often seen in many types of soils as a result of drying, especially due to fire (Doerr et al., 2000 and references therein). Furthermore, dried soil organic matter is more easily degraded than non-dried soil (Hayashi and Harada, 1969; Marumoto et al., 1977). Similarly, it is well known that the organic matrix of fruits and vegetables can collapse irreversibly after dehydration (Prothon et al., 2003). Here we use the drying effect on the sediment structure to investigate mechanisms of solute–solid sorption.

Sorption is a basic geochemical process that occurs at solid–water interfaces and influences the distribution, transport, and ultimate fate of organic substances in the environment (Stumm and Morgan, 1996). Sorption includes *ad*sorption onto a sorbent surface and *ab*sorption

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into a 3D sorbent matrix. The effects of water content on sorption of hydrophobic compounds by soil have been intensively studied (e.g. Yaron and Saltzman, 1972; Chiou and Kile, 1994; Borisover and Graber, 2002). The hydration effect is usually studied by comparing sorption of organic vapors by dried versus water-saturated soil, or by comparing sorption of organic compounds in organic solvents versus water. Sorption of hydrophobic organic compounds onto minerals is strongly depressed by the presence of water, as water outcompetes hydrophobic compounds for mineral surfaces due to the strong polarity of both minerals and water. In contrast, the effect of water suppression is much smaller in soil with a high organic content (like peat), and hydrophobic organic compounds are thought to be partitioned into the organic phase (Chiou and Shoup, 1985; Rutherford and Chiou, 1992; Chiou and Kile, 1994), although the mechanism often can be more complicated than the single partition model (e.g. Weber et al., 1992; Xing et al., 1996). Recent studies have hypothesized that water molecules can solvate polar portions of dried natural organic matter, creating new sorption sites (Graber and Borisover, 1998; Borisover and Graber, 2002). All these studies show the importance of water in the sorption behavior of soil. However, few studies have investigated sorption differences between hydrated soil/sediment and that which has been dried and then rehydrated using water as solvent. Moreover, in most studies of soil sorption, samples were usually dried first. This procedure could bias the results if the drying process itself causes irreversible changes.

Here we use the amino acid lysine to investigate sorption. Amino acid sorption in marine sediments (Christensen and Blackburn, 1980; Henrichs and Sugai, 1993; Wang and Lee, 1993; Montluçon and Lee, 2001) or on minerals (e.g. Hedges and Hare, 1987) has been well studied, and it is generally thought that sorption is controlled mainly by electrostatic interactions such as ion exchange. However, many questions about amino acid sorption are still unanswered. For example, how important are organic matter versus mineral phases to sorption? Is sorption due to *ad*sorption or *ab*sorption? In this study, we investigated the effects of drying on the sorption of organic compounds onto salt marsh sediments by comparing sorption capacities of dried (then rewetted) and fresh wet sediments; we use the results to further elucidate sediment sorption theory.

2. Methods

2.1. Sediment sampling and preparation

Sediment was collected from Flax Pond, a *Spartina alterniflora* salt marsh on the north shore of Long Island, NY. Flax Pond (FP) has been studied for many years, and its vegetation and circulation are well known (e.g. Woodwell et al., 1977). The sorption of organic matter onto sediments has been studied previously at this site (Wang and Lee, 1990, 1993; Montluçon and Lee, 2001). In the present study, surface (10 cm) sediments were sampled at various times throughout the year (March to November) by pushing core tubes into the sediment by hand in a non-vegetated area with relatively poorly sorted muddy sands. Sediment samples were homogenized with a mortar and pestle, and large objects (e.g., clamshells) and plant detritus larger than 2–3 mm were picked out by hand. Seawater from FP was filtered through a 0.2 μm Nylon filter for use in sorption batch experiments. We also measured sorption in coastal sediments for comparison. Coastal surface sediments (top ~10 cm) were taken in August, 2005 by box core from ~15 m water depth at the Northwest Control Station in central Long Island Sound (LIS) off New Haven, Connecticut (as in Aller, 1988). These sediments are dominated by silt and clay (Aller and Yingst, 1980). After being sampled, sediments were either immediately processed or refrigerated at 4 °C for several days until further processing. After the samples were well homogenized, some were dried in an oven at 60 °C overnight, and some were refrigerated at 4 °C. The dried samples were reweighed to quantify the water lost, and an equivalent amount of distilled water was added back to the samples. For convenience, dried and rewetted samples will be referred to as "dry/dried", and fresh or refrigerated samples as "wet".

2.2. Sorption experiments

2.2.1. Sorption measurements

To measure lysine sorption, about 0.5–1 g dry weight sediment was made into a slurry by adding 5–10 mL filtered seawater in a polypropylene centrifuge tube. The slurries were then poisoned with $HgCl_2$ (10 μg/mL) before use in batch experiments. In a previous study, Wang and Lee (1993) found no significant effect of $HgCl_2$ on sorption of amines or amino acids. Lysine was used as a sorbate because it is naturally found in marine sediments and soils and is strongly sorbed by sediment (Wang and Lee, 1993; Montluçon and Lee, 2001). Specific activity of ^{14}C-lysine added (Sigma) was 257 mCi/mmol. After spiking with ^{14}C-lysine, the slurry was vortexed until the sediment was well dispersed, and then shaken on a rotary table for 2 h. All experiments were conducted at room temperature (~25 °C). Samples were centrifuged at 6000 rpm (5900*g*) for 30 min, and 0.5–1 mL supernatant was removed for counting by liquid scintillation (Packard 1600CA). Sorption of lysine onto the wall of polypropylene centrifuge tubes was negligible. Lysine sorbed by the sediment was calculated by subtracting the amount in solution from the total amount of lysine added.

Lysine isotherms were measured by adding a wide range of ^{14}C-lysine concentrations to wet and dried FP sediments (about 0.5 g dry weight) in centrifuge tubes containing 5 mL seawater. The lysine concentration remaining in solution after sorption equilibrium ranged from 0.2 nM to 0.4 M. To use less radioactivity in samples where high lysine concentrations were added, we reduced the specific activity by adding unlabelled lysine to the ^{14}C-lysine.

Sorption isotherms for wet and dried sediment were obtained by measuring the amount of lysine sorbed at the different amounts of lysine added.

For comparison with lysine, the hydrophobic compounds tyrosine, aniline and naphthalene were also used as sorbates in a similar manner. Aniline is almost non-ionizable in slightly basic seawater (pH 7.8) (pK_a 4.6), as is also suggested by its low water solubility (3.4 g/100 mL, CRC Handbook, 1958). Naphthalene, a nonpolar compound, has even lower water solubility (0.003 g/100 mL, CRC Handbook, 1958) than aniline. Tyrosine is a relatively hydrophobic amino acid with a phenol functional group that is only slightly soluble at pH 7–8, about 0.048 g/100 mL (CRC Handbook, 1958). In contrast, lysine is very soluble in water. A fluorescence spectrophotometer (Hitachi F-4500) was used to quantify concentrations of these compounds in the supernatant (aniline, λ_{Ex} 300 nm, λ_{Em} 350 nm; naphthalene, λ_{Ex} 293 nm, λ_{Em} 336 nm; tyrosine, λ_{Ex} 287 nm, λ_{Em} 315 nm), based on standard curves. As in the lysine experiments, amounts sorbed to the sediment were calculated using mass balance calculations.

2.2.2. Lysine sorption by FP sediments with different treatments

The 3D structure of sediment may collapse upon drying, but may also be disrupted by the removal of organic matter. Boiling sediment or extracting it with EDTA can remove a portion of the organic matter, especially carbohydrates (e.g. Stevenson, 1994; Underwood et al., 1995). Different drying techniques may also affect the 3D structure. To investigate these possibilities, we compared lysine sorption on sediments that had been treated with various drying and extraction procedures. Samples of FP sediment collected in August, 2005 were oven-dried at 60 °C, desiccated at room temperature, or freeze-dried (−58 °C), or dried and then combusted overnight in a furnace at 450 °C. Wet samples were extracted with 10 mL of 0.2 M EDTA or immersed (with 10 mL seawater added) in a boiling water bath for 30 min. After the samples were centrifuged and the supernatant decanted, 10 mL seawater was added to rinse the extracted pellets, and then the pellets were used in sorption experiments. ^{14}C-lysine was added to centrifuge tubes containing the slurries (1 g of dried or extracted sediment and 10 mL seawater) for sorption experiments as described above.

2.2.3. Effect of pH and salinity on lysine sorption

For both wet and dried FP sediments, the pH of slurries was adjusted from 2.8 to 9.8 using 0.2 M HCl and 0.2 M NaOH. Then ^{14}C-lysine was added to the slurries following the sorption procedure described above. To test the effect of salinity on lysine sorption, 10 mL of distilled water was added to wet and dried sediments, and the slurries were shaken for 20 min. After centrifugation (5900*g*) for 10 min, the supernatant was decanted. This procedure was repeated 3 times. Seawater with different salinities (0, 2, 4, 9, 13, 26) was prepared by mixing different proportions of seawater and distilled water. Water of varying salinities was added to the rinsed sediment pellets to form slurries for sorption experiments, which were conducted as described above. Addition of ^{14}C-lysine generally resulted in concentrations of less than 5 nM after sorption was completed in these experiments.

2.2.4. Lysine sorption by size-fractionated FP sediments

Lysine sorption was also measured on size-fractionated sediments. Wet FP sediment samples were sieved into >300, 300–125, 125–63 and <63 μm fractions using stainless-steel mesh sieves. All the fractions except <63 μm were rinsed thoroughly with filtered seawater during fractionation to remove loosely attached finer materials. The >300 μm fraction was further fractionated in a settling column to separate sand and organic detritus based on their density difference. Organic detritus (OD) has much lower settling velocity than minerals, and floated at or near the top of the settling column, where it was collected for use as a sorbent. The sand fraction in the settling column was also used as a sorbent after thorough rinsing with filtered seawater until no organic particles were visible. Some of the fractionated material was oven-dried. About 0.5 g fresh or dried sediment and 5 mL seawater were mixed for batch experiments; 0.6 g sand and 12 mg OD (dry weight) were used as sorbents. Addition of ^{14}C-lysine resulted in less than 10 nM concentrations after sorption was completed. Carbon and nitrogen contents and surface areas of the different fractions were measured.

2.3. Cation exchange capacity and hydrophobicity of sediments

The cation exchange capacity (CEC) of wet and dried FP sediments was measured according to Rowell (1994). Briefly, 5 g (dry weight) of the wet and dried sediments were leached with 1 M alcoholic ammonium chloride overnight. These samples were then rinsed thoroughly with ethanol. The sorbed ammonium ions in the samples were exchanged with 2 M potassium chloride (KCl). Ammonium concentration in the KCl solution was measured according to Solórzano (1969), using indophenol blue manual colorimetry.

Water drop penetration time (WDPT) is a standard way to measure hydrophobicity of dry soils (e.g. King, 1981; Doerr et al., 2000). We measured the WDPT of fractionated dried and combusted (450 °C overnight) bulk and fractioned FP, and bulk LIS sediments. Briefly, about 5 water drops were dripped onto smoothed sediment samples. The time till the water drop visually penetrated the samples was recorded, and the average value of the 5 drops was used as WDPT.

2.4. Carbon and nitrogen, $\delta^{13}C$ and surface area measurements

Carbon and nitrogen contents were determined using a Carlo Erba model 1602 CNS analyzer after sediment

samples were dried and ground. Inorganic carbon was removed using 10% HCl, and carbonate content was generally less than 5% of total carbon. For this analyzer, precision for N is ±5%, and for C is ±2%. After the sediment was combusted by the CNS analyzer, CO_2 was collected to measure $\delta^{13}C$ by isotope ratio mass spectrometry according to Mak and Yang (1998).

Surface area of mineral grains was measured by nitrogen sorption with a Quantachrome surface area analyzer (Mayer et al., 1988). The grain size distribution of the <63 μm fraction was determined by the pipette method (Folk, 1974).

2.5. Sorption percent and solid–water distribution coefficient

Solid–water distribution coefficients (K_d) and sorption percents (%sorbed) are often used to assess the extent to which a compound is sorbed onto a solid phase. In this study, we mostly used nanomolar concentrations of lysine, but this and previous studies (Wang and Lee, 1993; Montluçon and Lee, 2001) showed that sorption of lysine is linear up to micromolar concentrations, and K_d and %sorbed are constant within this range. Thus

$$K_d = \frac{C_s}{C_d}, \tag{1}$$

$$\%\text{sorbed} = \frac{C_s \times \text{Mass}}{C_s \times \text{Mass} + C_d \times V}, \tag{2}$$

where C_s is the amount of sorbate associated with the sorbent (mole/kg); C_d is the concentration of sorbate in solution (mole/L); Mass is the total mass of sorbents in the batch (kg); V is the total volume of water in the batch (L). Combining (1) and (2) gives

$$\%\text{sorbed} = \frac{K_d}{K_d + V/\text{Mass}}. \tag{3}$$

Therefore, in a concentration range where the sorption isotherm is linear (through the origin), both K_d and %sorbed are constant if the same slurry ratios (V/Mass) are used. In this study, we kept lysine concentration within the micromolar range, and used the same slurry ratios in our experiments.

3. Results

3.1. Drying effects on sorption capacity of salt marsh sediment

Lysine sorption capacity was dramatically lower in Flax Pond (FP) sediments after they were dried. More than 90% of added lysine was sorbed by wet sediment while only ~20% was sorbed by dried sediment, and lysine concentrations were ~0.5 nM in wet sediment and ~4 nM in dried sediment after reaching equilibrium (Fig. 1). These percents sorbed are generally consistent with previous studies of lysine sorption in FP sediments (Wang and Lee, 1993; Montluçon and Lee, 2001). This experiment was repeated

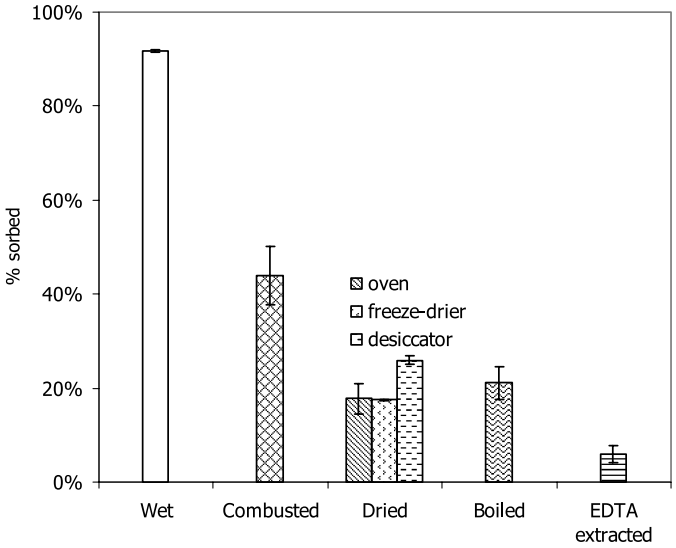

Fig. 1. Lysine sorption by Flax Pond sediment treated in different ways. Wet: fresh sediment; combusted: sediment combusted overnight in a furnace at 450 °C; dried (oven): sediment dried in oven at 60 °C; dried (desiccator): sediment dried at room temperature (25 °C); dried (freeze-drier): sediment lyophilized at −58 °C; boiled: sediment boiled in a water bath for 30 min; EDTA extracted: sediment extracted with 0.2 M EDTA at room temperature.

with sediment collected at different times of year (March to November) with similar results, although percents sorbed in wet sediment are generally higher in summer (~95%) than in winter (~85%). The length of time that sediments were rewetted (up to two months in $HgCl_2$ poisoned seawater as described above) did not alter sorption capacity; the original sorption capacity was never restored (data not shown). Different drying methods decreased sorption capacity of FP sediments by about the same amount, with desiccation at room temperature being slightly less effective (Fig. 1). However, when dried sediments were combusted, sorption capacity was significantly enhanced, increasing from 20% to 44%. Boiling in seawater lowered the sorption capacity of FP sediment by about the same amount as drying, and extraction with EDTA lowered it by slightly more.

In the linear range of lysine sorption, the distribution coefficient, K_d, was much higher (378 L/kg) in wet sediment than in dried sediment (2 L/kg), clearly showing that sorption capacity of wet sediment is much higher than that of dried sediment (Fig. 2). In contrast to lysine, sorption isotherms of tyrosine, aniline and naphthalene showed much lower sorption by wet than dried sediments (Fig. 2). There was not much sorption of tyrosine by wet FP sediment, while dry sediment sorbed about 40% of the added tyrosine, and the convex shape of the isotherm suggested that sorbed tyrosine increased the capacity for further sorption. Both wet and dried sediment sorbed more naphthalene than aniline, and the K_d of naphthalene was orders of magnitude higher than that of aniline. Using ^{14}C-naphthalene, Montluçon and Lee (2001) measured a K_d in wet sediments as 21 L/kg, similar to our result (17 L/kg) using fluorescence spectrophotometry.

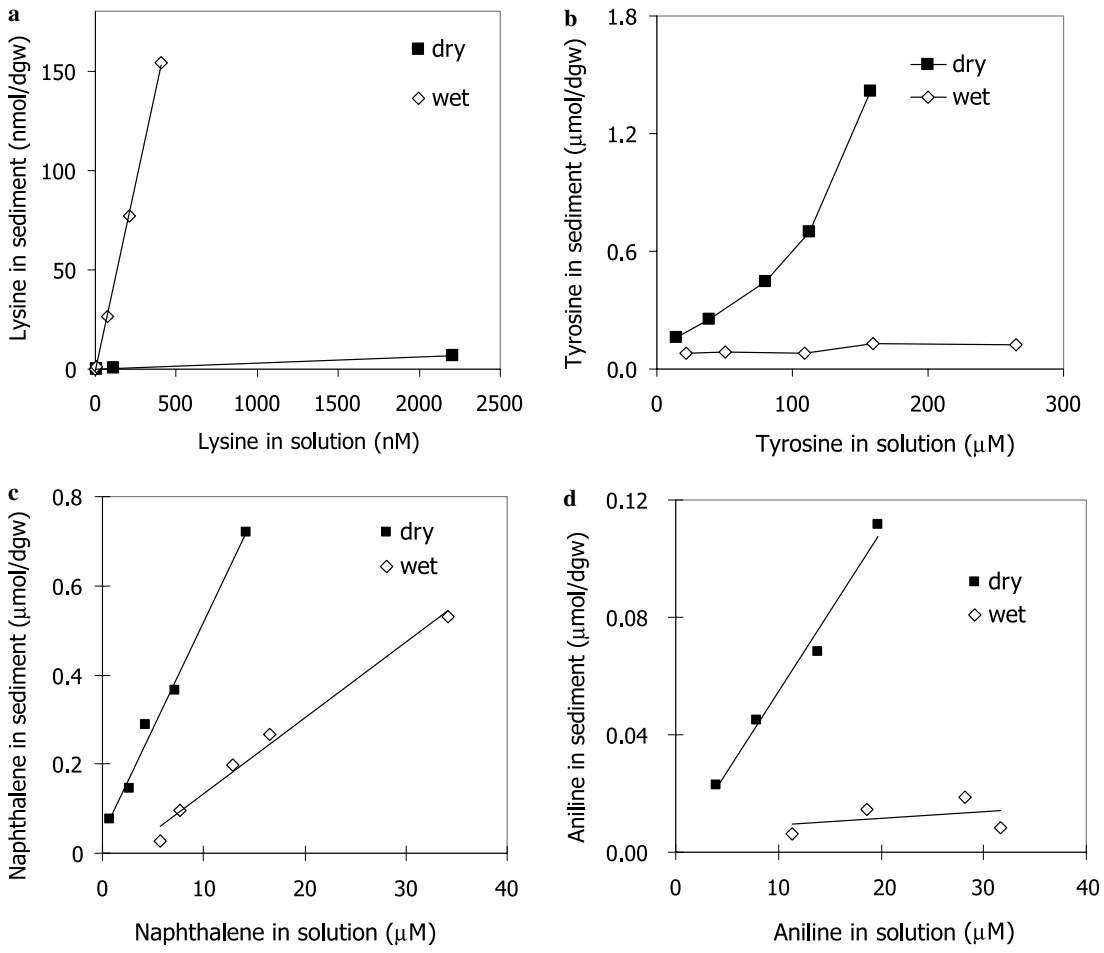

Fig. 2. Lysine, tyrosine, naphthalene and aniline sorption isotherms in wet and dried Flax Pond sediments. Solid lines are linear least square regression fits. (a) Lysine sorption: wet ($y = 0.3776x$, $r^2 = 0.9995$); dried ($y = 0.0032x$, $r^2 = 1$). (b) Tyrosine sorption. (c) Naphthalene sorption: wet ($y = 0.017x - 0.039$, $r^2 = 0.99$); dried ($y = 0.048x + 0.044$, $r^2 = 0.99$). (d) Aniline sorption: wet ($y = 0.0002x + 0.007$, $r^2 = 0.13$); dried ($y = 0.0054x + 0.0006$, $r^2 = 0.98$). The slope of the regression is the distribution coefficient K_d.

3.2. Sorption percents and isotherms in wet and dried FP sediments

Percents of lysine sorbed by wet and dried sediment beyond the linear range are shown by the open and closed triangles in Fig. 3. Initially, wet sediment sorbed much more (97%) of the lysine added than dried (22%) sediment did. In wet sediments, the percent lysine sorbed began to decrease when the amount of sorbed lysine reached 154 nmol/g dry weight; it continued to decrease until the sorbed lysine concentration in sediment reached 14 μmol/g (5%). At that point, the percent lysine sorbed began to increase, reaching a final value of 23% (1.2 mmol/g) at the last point tested. In dried sediments, only about 22% of the added lysine was sorbed at the low concentration range; this percent began to decrease slightly after lysine concentration reached 113 nmol/g, although lysine continued being sorbed by the sediment. In both wet and dried sediments, sorption isotherms and percent sorbed showed the same patterns once the concentrations of sorbed lysine reached about 2 μmol/g. Over the large concentration range tested, lysine sorption in wet sediment clearly cannot be quantitatively described by a single sorption model (e.g., linear, Langmuir, or Freundlich-type isotherm). This is frequently the case when dealing with a large sorbate concentration range or with natural organic matter as the sorbent (Schwarzenbach et al., 2003). At concentrations less than 154 nmol/g, lysine sorption in wet sediment can be well described by a linear isotherm ($C_s = 377.6C_d$, $n = 6$, $R^2 = 0.9995$) with K_d of 377.6 L/kg (see Fig. 3). From 154–14000 nmol/g, sorption sites appear to become filled, as both percent sorbed and K_d values dropped down with increasing concentrations of lysine in solution. Interestingly, lysine sorption was enhanced significantly after the solid sorbed about 1.4 μmol/g. In dried sediment, lysine sorption follows a linear-type isotherm in the range of 0–2 μmol/g ($C_s = 2.0C_d$, $R^2 = 0.9996$) with K_d of 2.0 L/kg. Similar to wet sediment, lysine sorption first decreased slightly after reaching 2 μmol/g, then began to increase, K_d reaching 2.3 L/kg at final point of 1 mmol/g.

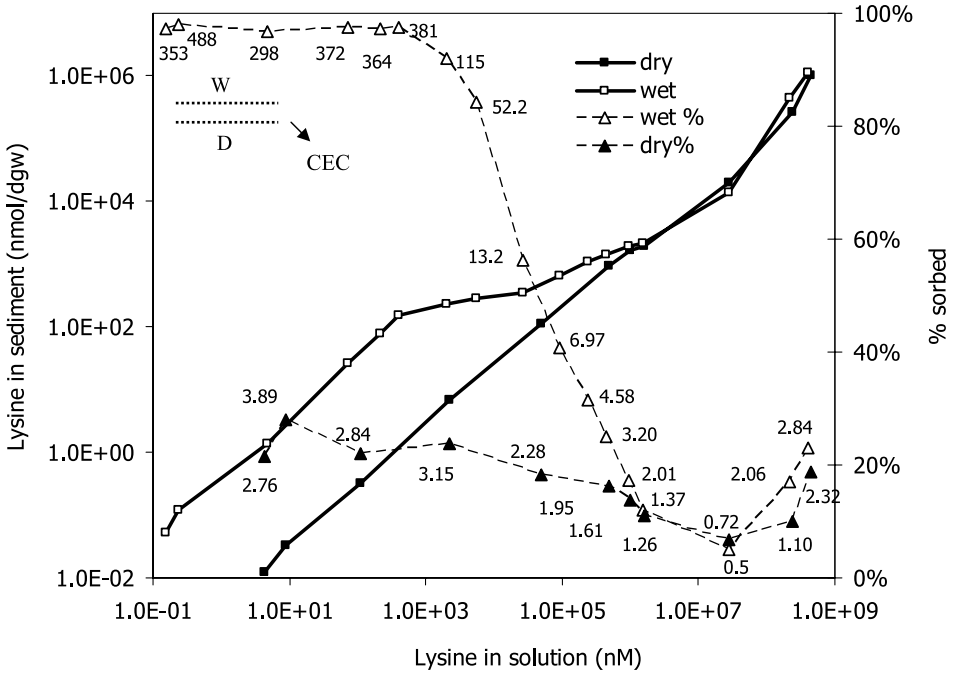

Fig. 3. Lysine sorption isotherms (boxes and solid lines) and percents lysine sorbed (triangles and dotted lines) in wet (open symbols) and dried (closed symbols) Flax Pond sediment. The numbers near the points on the dotted line represent the corresponding distribution coefficients (K_d, L/kg) at those points. The small horizontal lines in the figure are the cation exchange capacities (CEC) of wet (W) and dried (D) sediments. Experimental uncertainty of lysine sorption measurements (%sorbed) were generally within 1% (one standard deviation) for duplicate samples.

3.3. Effects of pH and salinity on lysine sorption

The impact of pH on lysine sorption was very different between wet and dried FP sediments (Fig. 4a). In wet sediment, percents of lysine sorbed were relatively high and constant (95–97%) over the pH range from 9.0 down to 5.8. Between 5.8 and 5.0, however, there was a dramatic change in sorption from 97% to 19%. In the pH range 5.8–5.0, the charge on lysine should be constant and positive since its pK_1 (α-COOH) is 2.18, pK_2 (α-NH_2) 8.95, and pK_R (residual amine) 10.79. Below 5.0, lysine sorption continued to decrease: at pH 2.8, only 5% of lysine added was sorbed. Above pH 9, sorption was also lower, dropping from 95% at pH 9 to 72% at pH 9.9. For dried sediment, however, we did not see a large pH effect, with sorption percent generally around 13%, although the sorption percent was slightly lower at lower pH (5.9–2.9) than at higher pH (9.7–5.9).

In addition to pH, salinity (or ionic strength) was also an important factor affecting lysine sorption to FP sediments (Fig. 4b). Lysine sorption by the wet sediment remained relatively constant (~89%) throughout the salinity range tested, 0–26.3, although there was a slight decrease with increasing salinity. In dried sediment, however, percent lysine sorbed decreased significantly with increasing salinity, from 94% at 0 to 28% at 25.9.

3.4. Lysine sorption on size-fractionated FP sediments and bulk LIS sediments

For bulk wet sediments, the percent of added lysine sorbed in Flax Pond sediments was slightly higher than LIS sediments, with about 96% sorption in FP versus 92% for LIS sediments (Fig. 5). Like FP sediment, wet LIS sediment had a higher sorption capacity than dried sediment, but by a smaller margin. Specific surface area (SSA) of FP sediment was 3.5 m^2/g and 11.1 m^2/g for LIS sediment. The FP and LIS sediments had similar organic carbon contents of 1.78% and 1.73%, respectively.

Lysine sorption percents on different size fractions of FP sediments are also shown in Fig. 5. The <63 μm fraction sorbed the largest amount of lysine under both wet and dry conditions. There were significant differences between wet and dried sediments in all size fractions, and the difference was largest in the smallest and largest size fractions. Using wet sediments, Wang and Lee (1993) observed that the <63 μm sediment fraction sorbed the most lysine, followed by the 300 μm to 1 mm fraction, consistent with this study. Organic detritus (OD) (>300 μm) also showed a significant decrease in sorption after being dried. We used 12 mg OD, which is half the amount used in sorption experiments with the >300 μm fraction. Less than 5% lysine was sorbed on the sand rinsed from the >300 μm fraction. No lysine sorption was found on a sand standard (600–850 μm Ottawa quartz, used directly without further treatment).

The >63 μm (sandy) fractions made up 68% of bulk FP sediment, while the <63 μm (silt–clay) fraction made up 32% (Table 1). Of the <63 μm fraction, 20% of the bulk was silt and 12% was clay. Specific surface areas of the different fractions varied from 0.5 to 6.9 m^2/g, with the smallest fraction having the largest surface area as expected (Table 1). Even though sands were the major weight

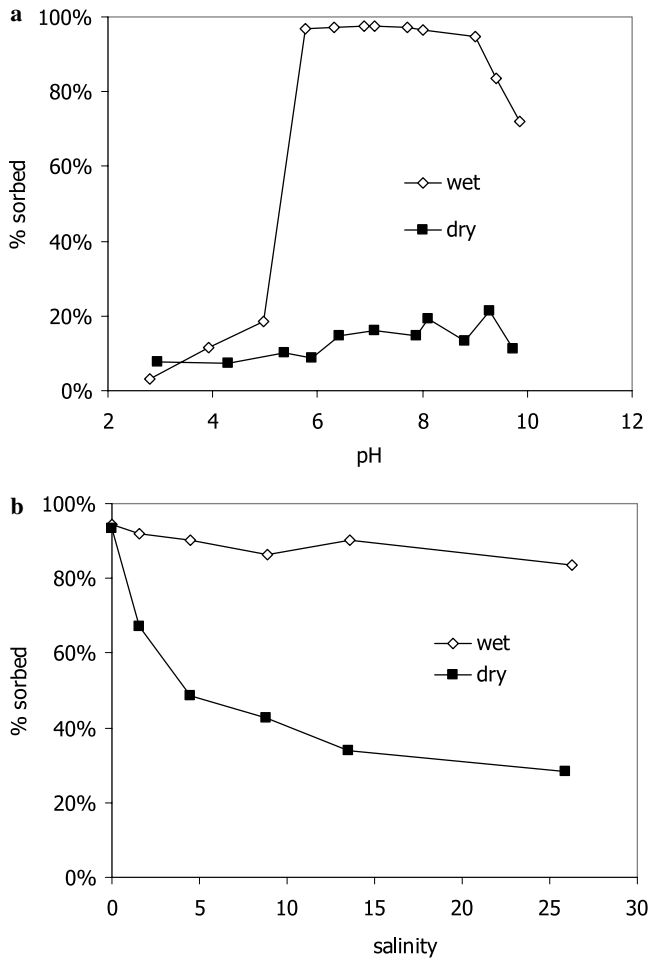

Fig. 4. Effects of pH and salinity on lysine sorption to wet and dried FP sediments. (a) pH effect; (b) salinity effect.

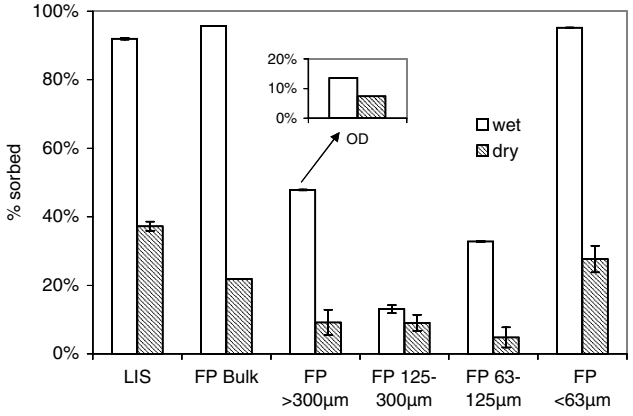

Fig. 5. Lysine sorption by bulk LIS sediments and different size fractions of Flax Pond sediments. Surface LIS sediment from central Long Island Sound off New Haven (15 m water depth). FP sediment was wet-fractionated using stainless steel meshes. Organic detritus was further fractionated from the >300 μm fraction using a settling column, and its sorption is shown in the inserted diagram.

fraction, clay and silt fractions provided about 82% of the surface area of bulk sediment. Organic carbon and nitrogen (CN) contents were most concentrated in the <63 μm fraction, and least in the 125–300 μm fraction (Table 1). C/N ratios in these fractions were lower in the smaller size fractions, with the >300 μm fraction having the highest (21.9) and <63 μm fraction the lowest (10.3) ratio. The $\delta^{13}C$ of fresh *Spartina* tissues was −13.5‰, consistent with other studies (Benner et al., 1991; Currin et al., 1995). OD was about 2‰ lighter than the fresh *Spartina*, and the >300 μm fraction was 2‰ lighter than the OD. Both the 125–300 μm and 63–125 μm had the same $\delta^{13}C$ (−19.5‰). The <63 μm fraction had about the same $\delta^{13}C$ as the bulk sediment, consistent with other salt marsh areas (Haines, 1976; Peterson et al., 1980; Currin et al., 1995).

Table 1
Organic carbon, nitrogen content, carbon isotopic composition and specific surface areas of each fraction in FP sediment

FP sediment	Weight percent (%)	N (%)	OC (%)	C/N	$\delta^{13}C$ (‰)	Surface area (m^2/g)
S. alterniflora	—	1.60	36.27	26.5	−13.50	—
OD >300 μm	—	1.20	34.77	33.9	−15.57	—
>300 μm	20.9	0.10	1.83	21.9	−17.75	0.54
125–300 μm	35.3	0.04	0.50	16.1	−19.50	0.55
63–125 μm	12.2	0.10	1.17	13.8	−19.50	1.48
<63 μm	31.7	0.28	2.49	10.3	−18.70	6.86
Bulk	—	0.15	1.78	13.5	−18.77	3.54

Based on the weight percent of each individual size fraction making up the bulk FP sediment (Table 1) and its associated K_d, we calculated integrated K_d values of 63.4 and 1.7 L/kg for wet and dried sediment, respectively, by adding up the K_ds of all the wet and dry fractions. The integrated K_d for wet sediment was lower than for bulk wet sediment (181 L/kg), while the integrated K_d for dried sediment was similar to bulk dried sediment (2.2 L/kg) (Table 1 and Fig. 5). Similarly, based on the CN content of each fraction and its corresponding weight percent, we can calculated the integrated CN content of the bulk sediment (N: 0.13%; C: 1.49%), which agrees well with the bulk values (N: 0.15%; C: 1.78%). This suggests that little material was lost during the fractionation process.

3.5. Cation exchange capacity and hydrophobicity of sediments

The cation exchange capacities (CEC) of wet and dried FP sediments were 445 and 187 μmol/dgw, respectively. Both these values fall within the range of representative CECs of surface soils, e.g. oxisols (50 μmol/dgw) to histosols (1400 μmol/dgw) (Sposito, 1989). However, the CEC in wet sediment was more than twice that of dried sediment. Clearly, the CEC of FP sediment is lowered by the drying process.

The water drop penetration time (WDPT) of dried FP sediments ranged from 2.6 s for the 300–125 μm fraction to 12.1 s for bulk sediment (Fig. 6). After being combusted, the WDPT dropped significantly to less than 2 s in all fractions. According to the repellency index by Dekker and

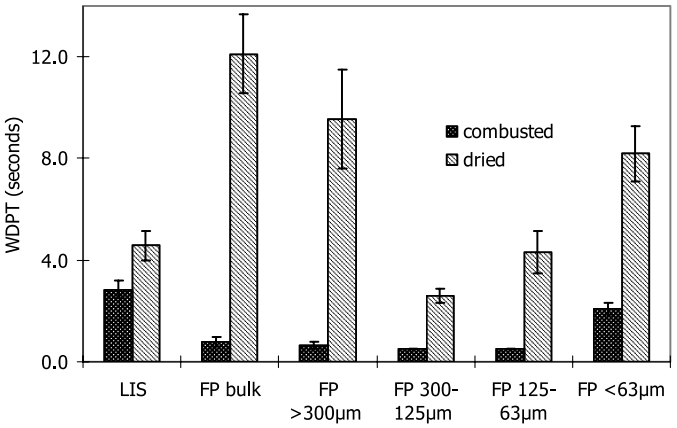

Fig. 6. Water drop penetration time (WDPT) of different size fractions of Flax Pond sediment and LIS sediment.

Ritsema (1994), dried <63 μm, >300 μm fractions and bulk sediment are slightly water repellent (5–60 s), while the 300–125 μm, 125–63 μm and all the combusted fractions are wettable (<5 s). LIS sediment had higher WDPT than FP sediment, yet showed a similar pattern, decreasing less after being combusted.

4. Discussion

4.1. Drying effects on salt marsh sediment

The sorption differences between lysine and the hydrophobic compounds, aniline, naphthalene, and tyrosine, in wet and dried sediments clearly indicate that sediments became more hydrophobic after being dried. Sorption of hydrophobic compounds usually involves non-specific van der Waals forces and hydrophobic effects, while electrostatic interaction and hydrogen bonding are considered major sorption mechanisms of hydrophilic compounds. Hydrophobic compounds sorb to organic matter rather than to mineral surfaces of natural solids because they cannot compete with water on the polar mineral surface (Chiou, 2002). If drying only reduces surface area, we would expect the same sorption pattern regardless of the polarity of the compound. Cation exchange capacity (CEC) decreased more than 50% when sediment was dried and rewetted, again indicating the change in sediment polarity.

Water drop penetration time (WDPT) measurements showed that dried sediments were more water-repellent than combusted sediments, suggesting that dried organic matter increased the hydrophobicity of sediment compared to a naked mineral surface. Consistently, combusted sediment showed higher sorption than dried sediment (Fig. 1). Wang and Lee (1993) found sorption of lysine by wet FP sediments decreased significantly after treatment with H_2O_2, showing the importance of organic matter to sorption. The importance of organic matter in sorption capacity was also suggested when EDTA extraction or boiling of wet sediment each resulted in the loss of as much or more sorption capacity as when wet sediment was dried. EDTA has been used to extract carbohydrate from sediment (Underwood et al., 1995; de Brouwer et al., 2003), possibly because it can break down the polymer gels by complexing their bridging cations (e.g., Ca^{2+} and Mg^{2+}) (Chin et al., 1998). Boiling sediment removes soluble organic matter like carbohydrates (Stevenson, 1994), and can also denature proteins due to the high temperature (McKee and McKee, 1999). Thus, EDTA extraction or boiling appears to remove a fraction of organic matter with strong sorption capacity. However, when we concentrated the EDTA and boiling extracts, they sorbed little lysine (data not shown). This suggests that the integrity of sedimentary organic matter structure plays an important role in sorption.

We observed clear differences between wet and dried (rewetted) sediments both visually and microscopically. Slurries with wet sediment have a gel-like appearance, while dried and rewetted sediment particles appear crystalline and angular. In addition, the volume of wet sediment was about twice that of dried (rewetted) sediment when the two were allowed to stand, although they had the same dry weight. This suggests that fresh sediment loses half of its water retention capacity when it is dried and does not regain it when rewetted. Gel-like particles with 3D structures (e.g., transparent exopolymers particles, or TEP) are abundant in seawater, and cations and acidic polysaccharides like uronic acids are important for stabilizing these gels (Alldredge et al., 1993; Chin et al., 1998; Verdugo et al., 2004). Uronic acid, thought to be important in gel formation, is also found in *Spartina*, possibly making up 15% of the total carbohydrates (Opsahl and Benner, 1999). Sedimentary organic matter, especially humic substances having abundant polar oxygen-containing functional groups like carboxyls, may also assemble into 3D organic structures in salt marsh sediment.

Drying could greatly affect the 3D nature of gel-like organic material. It has been well documented in the soil science literature that water repellency (hydrophobicity) is common in many types of soil, and is caused by conformational changes of organic molecules or to the release of waxes during fires or drying processes (Ma'shum and Farmer, 1985; Franco et al., 1995; Doerr et al., 2000). In food science, cellular structures of fruits and vegetables collapse during air-drying or osmotic drying; this process is irreversible, although the exact mechanism is not known (Prothon et al., 2003). Many properties (e.g., water binding capacity) of fresh fruits are significantly reduced by dehydration (Godeck et al., 2001; Vetter and Kunzek, 2002). In salt marsh sediment, polar groups on organic matter in seawater can eventually complex with dissolved metal ions, which cause them to physically extend into the solution. Hydrophobic groups, on the other hand, would coat mineral surfaces or coil in upon themselves or within an organic matrix to minimize their contact with water (Wershaw, 1993). When organic matter is dried, the loss of water forces polar portions of organic molecules to interact

with each other through forces like hydrogen bonding, and bend or twist in such a way that the non-polar groups are exposed outward (Ma'shum and Farmer, 1985; Doerr et al., 2000). Thus the drying process not only shrinks or collapses the 3D organic networks, but also may increase the hydrophobicity of the organic matter, thus changing the sorption properties of the sediment.

Rewetting dried sediment might release newly solubilized organic compounds, e.g., from biomass, which might interact with sorbates or affect sediment polarity. However, lysine sorption in dried sediment that was rinsed several times was still much lower than in wet sediments (see difference in sorption at seawater salinities in Fig. 4b). Consistently, little sorption was observed in concentrated supernatants from EDTA or boiling water extracts. Organic carbon and nitrogen contents in dried, rewetted sediment (after decanting the supernatant) were the same as wet sediment (data not shown). Thus, the polarity change of sediment after drying is probably caused by conformational changes of the sedimentary organic matter rather than to loss of an organic fraction during treatment.

4.2. Lysine sorption mechanisms

Previous studies have shown lysine sorption isotherms in wet sediment to be generally linear over natural concentration ranges (Henrichs and Sugai, 1993; Wang and Lee, 1993; Montluçon and Lee, 2001). Consistent with these past studies, we observed linear sorption isotherms in wet sediment below 400 nM (Fig. 1), suggesting that sorption energy is constant at these concentrations. Schwarzenbach et al. (2003) described two mechanisms that result in linear isotherms: when the sorbate is partitioned into a homogeneous organic phase, or when adsorption sites are far from being saturated (for example at low sorbate concentrations). Wet–dry sorption differences may help distinguish between these mechanisms. If we consider that the 3D structure of FP sediment organic matter collapses upon drying, as described above, lysine will no longer easily penetrate (or partition) into the structure, thus greatly depressing sediment sorption capacity. The large difference in lysine sorption between wet and dry FP sediments in the $<$400 nM concentration range suggests that collapse occurred and inhibited penetration. This difference suggests that absorption rather than adsorption is the dominant sorption mode over natural concentration ranges where the isotherm is linear. The K_ds in the linear range were at least one order of magnitude higher than in the non-linear range at high concentrations, suggesting that free sorption energy decreased dramatically. One possible explanation for this pattern is that different types of sites in wet sediment control lysine sorption. For example, highly active carboxyl groups could be responsible for linear sorption in the nanomolar range (see later discussion), and other relatively weak function groups (e.g., phenolic, quinolic or enolic) could be responsible for later sorption in the range of 154–2130 nmol/g range.

Partitioning of sorbate into a homogeneous organic phase is more probable for a hydrophobic sorbate than for hydrophilic lysine. However, cation exchange on sites within a 3D matrix more likely explains linear lysine absorption (sorbate partitioning between seawater and the 3D organic networks). Cation exchange has been suggested as a mechanism for basic amino acid sorption in clays (Hedges and Hare, 1987), marine sediments (Henrichs and Sugai, 1993; Wang and Lee, 1993), and soil (Stevenson, 1994). The fact that both lysine sorption and CECs are greatly depressed by drying (Fig. 3) suggests cation exchange is a major sorption mechanism in FP sediment. When the CEC is approached, the percent lysine sorbed in wet sediments plunges and the wet and dried sediment isotherms eventually merge.

The merging of wet and dried isotherms and the increase in percent sorbed suggest a new sorption mechanism at high lysine concentrations. The concentrations of sorbed lysine are much higher than the CECs of dried and wet sediments (Fig. 3). Schwarzenbach et al. (2003) suggest that a concave upward shape occurs when sorbed molecules modify the sorbent to favor further sorption (enhance the free energy of further sorption). Self-adsorption has been suggested for lysine sorption in organic-poor sediments, especially at millimolar concentrations (Henrichs and Sugai, 1993). Lysine has both negatively and positively charged groups as well as some hydrophobic character due to its relatively long carbon chain. Therefore, when a layer of lysine is adsorbed onto a surface, the surface may become more attractive for more layers of lysine to attach. Hedges and Hare (1987) also reported that sorption of basic amino acids by kaolinite is as strong as that by montmorillonite, although kaolinite has a much lower surface area and CEC. Their data are also consistent with self-sorption of lysine. Alternatively, lysine at such high concentrations might replace other sedimentary organic compounds, thus enhancing its sorption in sediment.

Salinity and pH are both important factors affecting lysine sorption. In wet sediment, the dramatic decrease in percent lysine sorbed between pH 5.8 and 5.0 (Fig. 4a) indicates that the surface charge of FP sediment must have changed significantly. Surface charges of minerals like smectite, feldspar or kaolinite are still negative within the pH range of 5.8–5.0 (Stumm and Morgan, 1996). In addition, adsorption of amino acids or other organic ions on minerals usually changes only slightly with pH (e.g., Dashman and Stotzky, 1982; Gu et al., 1994; Arnarson and Keil, 2000), so the effect of pH is more consistent with sorption by sedimentary organic matter than by minerals. Acidity of natural organic matter, in which humic substances are a major fraction, is usually dominated by the carboxyl (pK_a 4–6) and phenolic (pK_a 9–10) groups (Stumm and Morgan, 1996). Consistently, pH affects CEC of organic matter more strongly than of clays in soil (Stevenson, 1994). Therefore, carboxyl groups, either in positions near aromatic rings or on aliphatic side chains, are a reasonable

candidate for sorbing lysine in wet sediment, possibly through cation exchange.

At pH 5 or below, carboxyl groups would become protonated and lose their charge, thus losing their sorption capacity. H^+ attaches to COO^- more easily than does R–NH^{3+} due to the smaller proton ionic radius, and thus has much stronger cation exchange ability. The proposed ion exchange scheme in FP sediment is

$$\mathrm{OM{-}COO^-K^+ + NH_3^+{-}LYS \rightarrow OM{-}COO^-NH_3^+{-}LYS + K^+}$$

Where OM–COO^- represents the carboxyl groups in organic matter, K^+ represents the attached cations (possibly including K^+, Na^+, Ca^{2+} or Mg^{2+}), and NH_3^+–LYS represents the amine group of lysine. Above pH 9.0, amines lose a proton [pK_2(α-NH_2) 8.95, and pK_R 10.79 for the residual amine], so with less positive charge, less lysine was sorbed, as expected. In contrast, dried sediment was much less affected by pH. Together with the fact that the K_d of sorption in dry sediments is two orders of magnitude lower than in wet sediment, these results suggest that the sorption energy for the attachment of lysine to dried sediment is much lower, and that sorption in dried sediments involves weaker functional groups such as phenolic or enolic groups. The different effects of pH between wet and dried sediment indicate that drying might result in less access for lysine to carboxyl groups.

Lysine sorption in both wet and dried sediment was affected by salinity, and the effect was much greater in dried sediment than in wet sediment. This different pattern again suggested that lysine attached to different functional groups in wet and dried sediment. In wet sediment, sorption free energy of lysine is high enough as shown by K_d, so that major cations like K^+, Na^+, Ca^{2+} and Mg^{2+} can not compete with lysine for carboxyl groups. In dried sediment, however, sorption probably involves other types of functional groups with much lower sorption free energy, so major cations outcompete lysine for sorption sites. For example, in the salinity range 0–5, the percent of lysine sorbed decreased from 93% to 49% in dried sediment.

4.3. Drying effects on bulk and fractionated FP vs. LIS sediments

The percent lysine sorbed by various size fractions of wet Flax Pond sediment was related to the organic content of each fraction ($R^2 = 0.95$), with <63 μm sorbing the most and having the highest OC content, and 125–300 μm sorbing the least lysine and having the lowest OC content (Fig. 5), consistent with organic matter being the major sorbent in Flax Pond sediments. Lysine sorption in all size fractions including organic debris (OD) decreased significantly after being dried, with the 125–300 μm fraction showing the smallest degree of decrease, probably due to its low OC content. This is consistent with dried organic matter increasing the sediment hydrophobicity, with a concomitant decrease in lysine sorption. Likewise, the WDPT of all combusted sediment fractions were much lower than in dried sandy fractions, suggesting the presence of hydrophobic coatings on mineral surfaces, although it is also possible that combustion changes mineral morphology or oxidizes the minerals, which also might affect the WDPT (Valat et al., 1991).

The percents of lysine sorbed by wet FP sediments and wet LIS sediments were similar (Fig. 5). The carbon content of FP and LIS sediments is also about the same, but the specific surface area (SSA) is much lower in sand-dominated FP than in silt and clay dominated LIS. This again suggests that mineral surfaces in FP sediment played a limited role in lysine sorption, and sedimentary organic matter was responsible for sorbing lysine more strongly than LIS sediments. Dried LIS sediments sorbed more (37%) lysine than dried FP sediment (22%), suggesting that FP sediment organic matter was more altered by drying than LIS organic matter. A major source of organic matter in FP sediment is *S. alterniflora*, while organic matter in LIS sediment is heavily terrestrial in origin (Benoit et al., 1979). In sandy FP sediment fractions (>63 μm), C/N ratios ranged from 13.8 to 21.9, with OD having a C/N of 33.8, and $\delta^{13}C$ values for OD and *Spartina* were similar, showing that *Spartina* organic matter was especially important in larger size fractions.

Cellulose, hemicellulose and lignins polymers from *Spartina* that enter the sediment are subject to degradation processes including hydrolytic depolymerization (cellulose and hemicellose) and oxidation (lignins and lipids). During degradation, the polarity of organic matter may increase as the number of oxygenated functional groups increases. Enzymatic degradation causes free ends of lignin polymers to be oxidized to carboxylic groups (Wershaw, 1993; Kögel-Knabner, 2002). Carboxyl groups can also arise from the cleavage of aromatic rings of lignin (Stevenson, 1994). Novikova et al. (2002) found that the number of hydroxyl and carboxyl groups of lignin increase during composting, along with lignin's ion exchange capacity. Degraded or partially degraded organic polymers and monomers might be assembled with water and cations into 3D gel-like polar structures that can play a major role in sorption. When the 3D structures collapse and become more hydrophobic upon drying, the sorption capacity of sandy fractions would be severely depressed. Consistent with this, water repellency can be high in coarse-textured, sandy soils (Roberts and Carbon, 1972; Franco et al., 1995), and organic matter is thought to be the cause (Doerr et al., 2000).

Integrated K_d values for different size fractions are one-third the bulk K_d value in wet sediment. A CN budget suggested that little material was lost during sample fractionation, but we used filtered seawater to rinse fine materials through the mesh during fractionation, a process that might break up a 3D organic matrix, leading to decreased lysine sorption by individual fractions. This could explain the higher K_d in bulk than fractionated wet

sediments. On the other hand, integrated K_d and bulk K_d are similar in dried sediments, where we hypothesize that any gel-like structures have collapsed. Integrated and bulk surface areas from all the size fractions are 2.7 and 3.5 m^2/g, respectively (Table 1). In dried sediments, the ratios of integrated to bulk K_d and integrated to bulk surface area are the same, 1.23. This suggests that after sediment is dried, the loss of 3D structure results in lysine sorption to be mainly through adsorption onto solid surfaces.

5. Implications

Our sediment sorption results are consistent with the idea that a major contributor to the lysine sorption capacity in Flax Pond and Long Island Sound sediments is the 3D gel-like nature of the organic network originating from organic matter in *Spartina* and other vascular plants. We hypothesize that the 3D structures can exist separately as aggregates, or in association with minerals. Acidic functional groups within the 3D structure would be major sorption sites for lysine via cation exchange. Upon dehydration, organic molecules in the 3D structure would interact or associate with each other through forces like hydrogen bonding or van der Waals forces, and their nonpolar moieties would be exposed outward. As a result, the flexible 3D organic networks would shrink or collapse, becoming rigid and less polar. This rigidity change could have significant effects on sorption of organic contaminants (Leboeuf and Weber, 1997; Xing and Pignatello, 1997). Furthermore, we would expect seasonal changes in the mobility of sorbed organic matter. For example, hydrophobic organic contaminants absorbed into dried organic matter in soils might be released into solution during the rainy season or upon discharge into streams or the ocean due to increased polarity of organic matter. This also has important implications for sinking marine particles, as they are subject to osmotic pressure as they sink, which may also lead to dehydration (Prothon et al., 2003). For example, organic matter can be dehydrated to some degree when it is transferred from river to ocean due to salinity changes. Furthermore, this study suggests that results of sorption studies using dried soil or sediment might be biased due to the polarity change caused by drying.

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References

Alldredge, A.L., Passow, U., Logan, B.E., 1993. The abundance and significance of a class of large, transparent organic particles in the ocean. *Deep-Sea Res. Part I–Oceanogr. Res. Papers* **4** (6), 1131–1140.

Aller, R.C., 1988. *Benthic Fauna and Biogeochemical Processes in Marine Sediments*. Published on behalf of the Scientific Committee on Problems of the Environment (SCOPE) of the International Council of Scientific Unions (ICSU) by Wiley.

Aller, R.C., Yingst, J.Y., 1980. Relationships between microbial distributions and the anaerobic decomposition of organic-matter in surface sediments of Long Island Sound, USA. *Marine Biol.* **5** (1), 29–42.

Arnarson, T.S., Keil, R.G., 2000. Mechanisms of pore water organic matter adsorption to montmorillonite. *Marine Chem.* **7** (3-4), 309–320.

Benner, R., Fogel, M.L., Sprague, E.K., 1991. Diagenesis of belowground biomass of *Spartina alterniflora* in salt-marsh sediments. *Limnol. Oceanogr.* **3** (7), 1358–1374.

Benoit, G.J., Turekian, K.K., Benninger, L.K., 1979. Radiocarbon dating of a core from Long Island Sound. *Estuar. Coast. Marine Sci.* **9** (2), 171–180.

Borisover, M., Graber, E.R., 2002. Relationship between strength of organic sorbate interactions in NOM and hydration effect on sorption. *Environ. Sci. Technol.* **36** (21), 4570–4577.

Chin, W.C., Orellana, M.V., Verdugo, P., 1998. Spontaneous assembly of marine dissolved organic matter into polymer gels. *Nature* **391** (6667), 568–572.

Chiou, C.T., 2002. *Partition and Adsorption of Organic Contaminants in Environmental Systems*. Wiley-Interscience.

Chiou, C.T., Kile, D.E., 1994. Effects of polar and nonpolar groups on the stability of organic-compounds in soil organic-matter. *Environ. Sci. Technol.* **28** (6), 1139–1144.

Chiou, C.T., Shoup, T.D., 1985. Soil sorption of organic vapors and effects of humidity on sorptive mechanism and capacity. *Environ. Sci. Technol.* **19** (12), 1196–1200.

Christensen, D., Blackburn, T.H., 1980. Turnover of tracer (C-14, H-3 Labeled) alanine in inshore marine-sediments. *Marine Biol.* **58** (2), 97–103.

Currin, C.A., Newell, S.Y., Paerl, H.W., 1995. The role of standing dead *Spartina alterniflora* and benthic microalgae in salt-marsh food webs—considerations based on multiple stable-isotope analysis. *Marine Ecol. Progr. Ser.* **12** (1-3), 99–116.

Dashman, T., Stotzky, G., 1982. Adsorption and binding of amino acids on homoionic montmorillonite and kaolinite. *Soil Biol. Biochem.* **14** (5), 447–456.

de Brouwer, J.F.C., de Deckere, E.M.G.T., Stal, L.J., 2003. Distribution of extracellular carbohydrates in three intertidal mudflats in Western Europe. *Estuar. Coast. Shelf Sci.* **56** (2), 313–324.

Dekker, L.W., Ritsema, C.J., 1994. How water moves in a water repellent sandy soil. 1. Potential and actual water repellency. *Water Resourc. Res.* **30** (9), 2507–2517.

Doerr, S.H., Shakesby, R.A., Walsh, R.P.D., 2000. Soil water repellency: its causes, characteristics and hydro-geomorphological significance. *Earth-Sci. Rev.* **51** (1–4), 33–65.

Folk, R.L., 1974. *Petrology of Sedimentary Rocks*. Hemphill's.

Franco, C.M.M., Tate, M.E., Oades, J.M., 1995. Studies on non-wetting sands. 1. The role of intrinsic particulate organic matter in the development of water-repellency in non-wetting Sands. *Aust. J. Soil Res.* **33** (2), 253–263.

Godeck, R., Kunzek, H., Kabbert, R., 2001. Thermal analysis of plant cell wall materials depending on the chemical structure and pre-treatment prior to drying. *Eur. Food Res. Technol.* **213** (4–5), 395–404.

Graber, E.R., Borisover, M.D., 1998. Hydration-facilitated sorption of specifically interacting organic compounds by model soil organic matter. *Environ. Sci. Technol.* **32** (2), 258–263.

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. *Environ. Sci. Technol.* **28** (1), 38–46.

Haines, E.B., 1976. Relation between stable carbon isotope composition of fiddler crabs, plants, and soils in a salt marsh. *Limnol. Oceanogr.* **2** (6), 880–883.

Hayashi, R., Harada, T., 1969. Characterization of the organic nitrogen becoming decomposable through the effect of drying of a soil. *Soil Sci. Plant Nutr.* **15** (5), 226–234.

Hedges, J.I., Hare, P.E., 1987. Amino acid adsorption by clay minerals in distilled water. *Geochim. Cosmochim. Acta* **51** (2), 255–259.

Henrichs, S.M., Sugai, S.F., 1993. Adsorption of amino acids and glucose by sediments of Resurrection Bay, Alaska, USA: functional group effects. *Geochim. Cosmochim. Acta* **57** (4), 823–835.

Hodgman, C.D., Weast, R.C., Selby, S.M. (Eds.), 1958. *CRC Handbook of Chemistry and Physics*, 40th ed. Chemical Rubber Publishing Co., Cleveland, Ohio.

King, P.M., 1981. Comparison of methods for measuring severity of water repellence of sandy soils and assessment of some factors that affect its measurement. *Aust. J. Soil Res.* **19** (4), 275–285.

Kögel-Knabner, I., 2002. The macromolecular organic composition of plant and microbial residues as inputs to soil organic matter. *Soil Biol. Biochem.* **34** (2), 139–162.

Leboeuf, E.J., Weber, W.J., 1997. A distributed reactivity model for sorption by soils and sediments. 8. Sorbent organic domains: discovery of a humic acid glass transition and an argument for a polymer-based model. *Environ. Sci. Technol.* **31** (6), 1697–1702.

Ma'shum, M., Farmer, V.C., 1985. Origin and assessment of water repellency of a sandy south Australian soil. *Aust. J. Soil Res.* **23** (4), 623–626.

Mak, J.E., Yang, W.B., 1998. Technique for analysis of air samples for C-13 and O-18 in carbon monoxide via continuous-flow isotope ratio mass spectrometry. *Anal. Chem.* **70** (24), 5159–5161.

Marumoto, T., Kai, H., Yoshida, T., Harada, T., 1977. Dry effect on mineralization of microbial cells and their cell walls in soil and contribution of microbial cell walls as source of decomposable soil organic matter due to drying. *Soil Sci. Plant Nutr.* **23** (1), 9–19.

Mayer, L.M., Macko, S.A., Cammen, L., 1988. Provenance, concentrations and nature of sedimentary organic nitrogen in the Gulf of Maine. *Marine Chem.* **25** (3), 291–304.

McKee, T., McKee, J.R., 1999. *Biochemistry: An Introduction*. WCB/McGraw-Hill.

Montluçon, D.B., Lee, C., 2001. Factors affecting lysine sorption in a coastal sediment. *Org. Geochem.* **32** (7), 933–942.

Novikova, L.N., Medvedeva, S.A., Volchatova, I.V., Bogatyreva, S.A., 2002. Changes in macromolecular characteristics and biological activity of hydrolytic lignin in the course of composting. *Appl. Biochem. Microbiol.* **38** (2), 181–185.

Opsahl, S., Benner, R., 1999. Characterization of carbohydrates during early diagenesis of five vascular plant tissues. *Org. Geochem.* **30** (1), 83–94.

Peterson, B.J., Howarth, R.W., Lipschultz, F., Ashendorf, D., 1980. Salt-marsh detritus—an alternative interpretation of stable carbon isotope ratios and the fate of *Spartina alterniflora*. *Oikos* **34** (2), 173–177.

Prothon, F., Ahrne, L., Sjoholm, I., 2003. Mechanisms and prevention of plant tissue collapse during dehydration: a critical review. *Crit. Rev. Food Sci. Nutr.* **43** (4), 447–479.

Roberts, F.J., Carbon, B.A., 1972. Water repellence in sandy soils of southwestern Australia. 2. Some chemical characteristics of hydrophobic skins. *Aust. J. Soil Res.* **10** (1), 35–42.

Rowell, D.L., 1994. *Soil Science: Methods and Applications*. Longman Scientific & Technical.

Rutherford, D.W., Chiou, C.T., 1992. Effect of water saturation in soil organic matter on the partition of organic compounds. *Environ. Sci. Technol.* **26** (5), 965–970.

Schwarzenbach, R.P., Gschwend, P.M., Imboden, D.M., 2003. *Environmental Organic Chemistry*. Wiley.

Solórzano, L., 1969. Determination of ammonia in natural waters by phenolhypochlorite method. *Limnol. Oceanogr.* **14** (5), 799–801.

Sposito, G., 1989. *The Chemistry of Soils*. Oxford University Press.

Stevenson, F.J., 1994. *Humus Chemistry: Genesis, Composition, Reactions*. John Wiley & Sons.

Stumm, W., Morgan, J.J., 1996. *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters*. Wiley.

Underwood, G.J.C., Paterson, D.M., Parkes, R.J., 1995. The measurement of microbial carbohydrate exopolymers from intertidal sediments. *Limnol. Oceanogr.* **40** (7), 1243–1253.

Valat, B., Jouany, C., Riviere, L.M., 1991. Characterization of the wetting properties of air-dried peats and composts. *Soil Sci.* **152** (2), 100–107.

Verdugo, P., Alldredge, A.L., Azam, F., Kirchman, D.L., Passow, U., Santschi, P.H., 2004. The oceanic gel phase: a bridge in the DOM-POM continuum. *Marine Chem.* **92** (1–4), 67–85.

Vetter, S., Kunzek, H., 2002. Material properties of processed fruit and vegetables. II. Water hydration properties of cell wall materials from apples. *Eur. Food Res. Technol.* **214** (1), 43–51.

Wang, X.C., Lee, C., 1990. The distribution and adsorption behavior of aliphatic amines in marine and lacustrine sediments. *Geochim. Cosmochim. Acta* **54** (10), 2759–2774.

Wang, X.C., Lee, C., 1993. Adsorption and desorption of aliphatic amines, amino acids and acetate by clay minerals and marine sediments. *Marine Chem.* **44** (1), 1–23.

Weber, W.J., Mcginley, P.M., Katz, L.E., 1992. A distributed reactivity model for sorption by soils and sediments. 1. Conceptual basis and equilibrium assessments. *Environ. Sci. Technol.* **26** (10), 1955–1962.

Wershaw, R.L., 1993. Model for humus in soils and sediments. *Environ. Sci. Technol.* **27** (5), 814–816.

Woodwell, G.M., Whitney, D.E., Hall, C.A.S., Houghton, R.A., 1977. Flax Pond ecosystem study—exchanges of carbon in water between a salt marsh and Long Island Sound. *Limnol. Oceanogr.* **22** (5), 833–838.

Xing, B.S., Pignatello, J.J., 1997. Dual-mode sorption of low-polarity compounds in glassy poly(vinyl chloride) and soil organic matter. *Environ. Sci. Technol.* **31** (3), 792–799.

Xing, B.S., Pignatello, J.J., Gigliotti, B., 1996. Competitive sorption between atrazine and other organic compounds in soils and model sorbents. *Environ. Sci. Technol.* **30** (8), 2432–2440.

Yaron, B., Saltzman, S., 1972. Influence of water and temperature on adsorption of parathion by Soils. *Soil Sci. Soc. Am. Proc.* **36** (4), 583–586.