Adsorption of short-chain organic acids onto nearshore marine sediments

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Abstract—The adsorption of acetate, butyrate, lactate, and stearate was measured using a clastic mud from Cape Lookout Bight, N.C. (CLB), a lateritic muddy sand from Kahana Stream, Oahu, Hawaii (KS), and a fine carbonate sand from Waimanalo Beach, Oahu, (WB). Partition coefficients (Kd, moles adsorbed per g of solid phase/moles dissolved per ml of porewater) ranged from 10^2 to <10^-3, and displayed the following trends: CLB > KS > WB, and stearate > acetate > butyrate > lactate. The percent adsorption of the sediment organic acid pools showed similar trends: stearate, 99%; acetate, 9–23%; butyrate, 5–23%; lactate, <0.2–7%. These results reflected the relatively nonpolar nature of the sand surfaces in WB and KS sediments, and the polarities of the organic acids. Kd was approximately constant for each organic acid-sediment combination over a dissolved organic acid concentration range of 10^2, using concentrations between 1M and 10^-14 M. This constancy over a wide porewater concentration range suggested that adsorption was not limited by the availability of surface adsorption sites.

INTRODUCTION

ORGANIC MATTER decomposition in marine sediments is an important biogeochemical process which remains incompletely understood, and as a result there is much interest in increasing our understanding of the reaction pathways and rates. Techniques have therefore been developed to measure the very low concentrations of small organic acid (OA) intermediates involved in the terminal decomposition reactions of organic matter in sediments and their porewaters (e.g., ANSBÆK and BLACKBURN, 1980; BARCELONA et al., 1980; SANSONE and MARTENS, 1981b). However, these methods either (a) measure only the porewater concentrations, or (b) measure the whole-sediment concentration without discriminating between porewater pools and those associated with the sediment solid phase.

Methods have also been developed for the measurement of apparent turnover rates of these terminal degradation intermediates in sediments (e.g., ANSBÆK and BLACKBURN, 1980; SANSONE and MARTENS, 1981b; LOVLEY and KUG, 1982; SANSONE, 1986). However, these rates must be termed "apparent" (SANSONE and MARTENS, 1981a) because they are derived from substrate concentration measurements described above, which may not directly reflect the substrate bioavailability. Calculation of actual turnover rates would require a knowledge of the amount of the whole sediment substrate concentration which is available to the responsible microorganisms, data that are currently unknown. For example, studies by CHRISTENSEN and BLACKBURN (1982), SHAW et al. (1984), and PARKE et al. (1984) have indicated that a significant portion of the analytically measurable acetate in marine sediments may not be available to anaerobic bacteria for metabolism. The cause of this phenomena, however, remains unknown.

The bioavailability of organic compounds in sediments is closely related to the distribution of these compounds between porewater (in both free and complexed form) and the solid phase (BRINK et al., 1980). It has been shown for several organics that solid phase interactions can diminish to varying degrees the availability of the compounds to microorganisms, presumably by raising the energy required to transport the compounds into the cells (e.g., STOTZKY, 1980).

To our knowledge the question of the bioavailability of adsorbed organic substrates has not been addressed in the literature in any quantitative fashion, although some qualitative data are available. STOTZKY (1980) reported that proteins complexed directly onto clay particles were not available to microbes, but those adsorbed to other previously bound proteins on the clays were utilized. FLETCHER et al. (1980) concluded that organics located within clay layers would not be available to bacteria or higher organisms.

Previous adsorption studies

Early work on the adsorption of organic compounds on surfaces was conducted with standard surfaces such as silica gel, carbon black, graphite, and activated charcoal (see review by KIPLING, 1965). However, the applicability of these studies to systems with non-standard surfaces such as natural sediments with organic coatings (e.g., SUSS, 1973) has been questioned (DAVIS, 1982). THENG (1974) concluded that short-chain organic acids (SCOAs) would interact with the exchangeable calcium ions on the surface of clay minerals via the SCOA carboxyl groups. However, HOFFMANN and BRINDLEY (1960) observed that a chain length of at least five carbons was necessary for non-charged organics to adsorb appreciably onto montmorillonite from dilute solution. Also, HAMAKER and THOMPSON (1972) and BURNS (1980) have noted that the maximum adsorption of long-chain OAs is generally at a higher pH in soils than the pK_a of the individual acids; this was attributed to the fact that the "solution pH" of a soil may not adequately describe the conditions present at the solid/liquid interface, particularly when clay minerals are involved. It appears that empirical approaches offer the best hope at this point for understanding the adsorption of specific organic compounds on natural sediment surfaces.
Organic coatings have been shown to play a major role in soil and sediment adsorption of hydrophobic organic compounds (e.g., SCHWARZENBACH and WESTALL, 1981; WU and GSCHWEND, 1986) and metals (e.g., DAVIS and LECKIE, 1981), but there is little data for hydrophilic organic compounds. Organic coatings on solid surfaces may take the form of multiple layers due to the apparent preference of dissolved organic compounds to adsorb to bound organic matter rather than to clean mineral surfaces (STOTZKY, 1980). This phenomenon has been reported in studies of the adsorption of amino acids onto marine sediments (ROSENFELD, 1979) and natural dissolved organic matter onto metal oxides and clay minerals (DAVIS, 1982).

Benjamin and Leckie (1981) have stressed the need of performing adsorption experiments over a wide range of concentrations in order to accurately predict behavior in natural systems; they found that a relatively few number of highly active, quickly saturated sites dominated metal adsorption on a pure oxide surface.

This study

There were four main objectives of this research. First, we wished to measure the distribution of several SCOAs between the porewater and the solid phase in three very different types of marine sediment: a clastic mud, a lateritic muddy sand, and a fine carbonate sand. It was hoped that this range of solutes and absorbents would provide information on the main factors controlling adsorption in natural sediments. Second, we wished to calculate adsorption coefficients for the SCOAs and sediments studied. Third, we hoped to use the coefficients to provide information on the mechanisms of adsorption. For example, coefficients that decrease with increasing SCOA concentration would indicate a saturation of adsorption sites. Fourth, we wished to estimate an upper limit on the degree to which adsorption lowers the bioavailability of SCOAs with a fixed trace amount of the corresponding 14C-labelled SCOA. The samples were shaken, centrifuged, and sub-sampled for measurement of 14C-activity in the supernatant and in the sediment. Partition coefficients were computed using a knowledge of the water content in the centrifuged sediment, and of the distribution of radioactivity between the supernatant and solid phase subsamples.

Only short-term (approximately 20 min) experiments were performed in this study because of the difficulties in keeping the sediments sterile over significantly longer periods. Loss of sterility would lead to rapid microbial consumption of the very labile SCOAs, and result in ambiguous data. Consequently we could not discriminate between the mechanisms of adsorption and absorption in these experiments, although for convenience we will only use the former expression in this paper.

MATERIALS AND METHODS

Sample collection and description

Three different marine sediments were used in these experiments; the bulk properties are listed in Table 1. The first sediment type was an anoxic clastic mud obtained during the midsummer months of 1983 and 1984 from station A-1 in Cape Lookout Bight, North Carolina (CLB; for a description of this site see MARTENS and KLUMP, 1980). Samples were collected from the top 10 cm of sediment by a scuba diver using a large bucket. After collection the forty-liter composite samples were manually homogenized, transferred to 500-ml glass bottles fitted with teflon-lined screw caps, and refrigerated at 4°C for the subsequent air shipment to our laboratory in Hawaii. Upon arrival, sediment samples were sterilized by gamma-ray irradiation of at least 2.5 Mrad (ca. 14.5 h) using a 10,000 Curie Co-60 source (Hawaii Research Irradiator, University of Hawaii at Manoa). These bottles of anoxic, sterile CLB sediments were stored at 0–4°C until adsorption experiments were conducted; no visual evidence of sediment oxidation was noted.

The other two types of sediment were collected from nearshore locations on the island of Oahu, Hawaii. Fine carbonate beach sand was obtained by a diver from the surface sediments just outside the surf zone (approximately 1.5–3 m water depth) at Waimanalo Beach (WB). Samples of this aerobic sediment were wet sieved through a 350 μm mesh screen using seawater from the site, and then transported (about 45 min) to our Honolulu-based laboratory for irradiation as described above. The Kahana Stream (KS) sediment was obtained from an estuarine embayment fed by a small mountain stream. Samples were taken from a depth of 0–20 cm into the lateritic muddy sand by driving a PVC core tube (8.5 cm o.d.) into the sediment. The cores were transported (about 45 min) to our laboratory, where large particulate debris was manually removed and the core samples homogenized after discarding.

<table>
<thead>
<tr>
<th>Site</th>
<th>Organic C</th>
<th>Inorganic C</th>
<th>X H₂O</th>
<th>Surface Area</th>
<th>Mineralogy</th>
<th>Grain Size</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(g dry weight, g/q)</td>
<td>(g/q)</td>
<td>(m²/g)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CLB</td>
<td>3.5</td>
<td>0.02</td>
<td>68</td>
<td>14</td>
<td>Aluminosilicates</td>
<td>Clay</td>
</tr>
<tr>
<td>KS</td>
<td>1.3</td>
<td>5.8</td>
<td>45</td>
<td>25</td>
<td>Ca(Mg)CO₃ (15-20 mole % Mg), aragonite, kaolinite-metahalloysite, amorphous</td>
<td>Fine sand + Fe-oxides</td>
</tr>
<tr>
<td>WB</td>
<td>0.17</td>
<td>11</td>
<td>29</td>
<td>1.3</td>
<td>Ca(Mg)CO₃ (10-15 mole % Mg), fine - very fine sand</td>
<td></td>
</tr>
</tbody>
</table>

Table 1. Bulk sediment properties.
the brown oxidized surface layer (generally the top 2–3 cm); samples were then irradiated as described above. Porowater salinity from the KS site ranged between 16 and 20‰, with the near-surface porowater being generally less saline than that found deeper in the core.

The whole-sediment pH values were: CLB, 7.0; WB, 8.1; KS, 7.7. Irradiation of the sediments did not cause significant changes in the pH (data not shown).

Adsorption experiments

For each experiment, a sediment sample was added to each of 5 or 6 tared, 50 ml polypylene screw-cap centrifuge bottles (Corning 25330) using a plastic syringe with the barrel end removed to form an open-ended cylinder. The tubes were then gamma-ray irradiated as described above. Transfers of CLB sediment were conducted under anaerobic conditions by use of a controlled atmosphere glove box (Kewaukee Scientific, Lockhart, Texas) filled with O₂-free argon. Sediment-filled centrifuge tubes were placed in one-liter glass screw-cap bottles before removal from the glove box so that the sediment would not oxidize during subsequent gamma irradiation. The irradiated samples were returned to the glove box for further processing. WB samples were handled under ambient atmosphere since they were not obtained from an anoxic environment. The KS sample tubes were purged of O₂ by use of a slow stream of argon gas before irradiation in order to maintain a relatively O₂-free environment during irradiation.

Two slightly different methodologies were used for the preparation of sediment slurries and the measurement of radioactivity in the sediment pellets. In the earlier stages of this research 30–40 cm³ of sediment plus 10–20 ml of overlying seawater (sparged with Ar for CLB sediment) were added to each tube before sterilization (Method A). For later experiments each replicate of 1-ml sediment subsamples (which the weight of the sediment pellet was recorded. The sediment pellet was manually homogenized before further processing. In method A, the labelled SCOA from triplicate 1-g pellet subsamples was extracted from the sediment particles into Aquasurvey by repeated vortexing and sonication before liquid scintillation counting. Quench curves were prepared for each experiment to account for quenching and efficiency corrections. In method B, three 0.5-g replicate pellet subsamples were dispensed into film tubes (Nalge 500–1000) which were then sealed and rolled to fit into size 0 gelatin capsules. ¹⁴C-labelled organic compounds associated with the sediment phase were oxidized to ¹⁴CO₂ and subsequently trapped in a CO₂-absorbing scintillant (Oxyfluor, NEN) using an Intertechnique Oxymat (INUS Corp., Fairfield, New Jersey). Samples were corrected for the Oxymat recovery efficiency (88–96%).

Solution preparation and concentrations

Serial dilutions of a concentrated stock solution of each SCOA were made using UV-oxidized seawater collected from each particular site; stock solution pH was adjusted to 8.0 with 20% Na₂CO₃. For each experiment, 5 to 6 sediment tubes were prepared, each receiving a different concentration of SCOA solution. A tube which contained only UV-oxidized seawater served as a control. The concentrations of the solutions added ranged between 500 mM and 5 μM for acetate, 50 mM and 10 μM for butyrate, and 40 mM and 2 μM for lactate. A total of 0.11 μCi of ¹,²-¹⁴C-sodium acetate (ICN Pharmaceuticals, Inc.; 55.5 mCi mmol⁻¹), 0.062 μCi of 1,2,³-¹⁴C-sodium lactate (ICN, 90 mCi mmol⁻¹), or 0.06 to 0.07 μCi of ¹,²-¹⁴C-sodium butyrate (Amersham, 56 mCi mmol⁻¹) were added to each tube in method A. In method B, 0.05 μCi of ¹⁴C-butyrate or 0.02 μCi ¹⁴C-acetate were added per sediment tube. All solutions were filter-sterilized or gamma-irradiated before addition to sediment samples.

The effect of gamma-irradiation on the SCOA concentrations was determined as follows. Acetate (900 μM), butyrate (1.1 mM), and lactate (4.1 mM) solutions were prepared in UV-oxidized distilled water, brought to pH 10.0 with 5% Na₂CO₃, and filter-sterilized with 0.45 μm Millipore inline filters. Aliquots of each solution were dispensed into sterile, combusted 1-ml vials sealed with Teflon-lined septa, and then gamma-irradiated with exposures ranging from 0 to 5.8 MRad. Non-irradiated controls for each treatment were maintained at 16°C (the temperature within the gamma-irradiator) during the 0–30 h irradiation periods. All solutions were freeze-dried prior to analysis. Acetate and butyrate samples were derivatized overnight with methanolic-HCl (SANSONE and MARTENS, 1981b). The resulting SCOA methyl esters were determined using a Varian 3700 gas chromatograph interfaced with a Finnigan MAT model 700 Ion Trap Detector. Lactate concentrations were determined using a Dionex 4000i ion chromatograph. After 5.8 MRad exposure 5% of the original acetate remained; after 4.5 MRad exposure 28% of the original butyrate remained; after 4.6 MRad exposure 52% of the original lactate remained (data not shown). These data were used to estimate the resulting concentrations of acetate, butyrate, and lactate solutions that were gamma-irradiated before addition to sediment samples.

Gamma irradiation time-course experiments

In order to find the dosage necessary to sterilize our sediment samples, the rate of microbial oxidation of ¹⁴C-labelled acetate in our sediments was measured (SANSONE and MARTENS, 1981b) after different gamma ray exposures. Briefly, 3 ml of fine-grain carbonate sediment collected from Kanehoe Bay, Oahu were placed into sterile, 15-ml Vacutainer culture tubes to which 1 ml of sterile, sulfate-free artificial seawater and 0.2 μCi of ¹⁴C-acetate were added. Triplicate samples were gamma irradiated between 0 and 16.5 h (0.3 to 4.87 MRad, respectively), after which an acid-formalin solution was added to terminate the incubation. Microbially-produced ¹⁴CO₂ was trapped on filters wetted with Protosol (NEN), and the radioactivity counted to generate a time-course of acetate turnover vs. dose of gamma irradiation. Acid formalin-killed controls were used to correct for any chemically-produced ¹⁴CO₂.

Microbial activity was eliminated with 2.3 MRad of radiation (Fig. 1). Consequently, adsorption experiments were conducted with sediment samples that had been irradiated for at least 2.5 MRad.

Adsorption control experiments

Adsorption isotherms were also generated for stearate, a surface-active fatty acid known to adsorb readily to carbonate minerals (SUSS, 1970), as a verification of the experimental protocol. The adsorption of stearate onto KS and CLB sediments was monitored following the procedures of method B, with the exception that in the CLB experiment only 1 ml of unlabelled stearate solution was added to each tube. Sodium stearate solutions were prepared in methanol and subsequently diluted with UV-sterilized seawater to yield concentration

Sediment adsorption of organic acids

1891
The activity in the solid phase was then normalized to the mass of dry sediment:

\[
\text{dpm adsorbed} = \frac{S}{g \text{ dry sediment}} - (E - (Ed)).
\]  

A mass balance of the added radiotracer was calculated at the end of each experiment. Data were only used from experiments in which we could recover 72–150% of the added label in the sum of the following pools: wet sediment, overlying water, and adsorbed to the centrifuge tube wall (stearate only).

**Bulk sediment analyses**

Organic carbon was determined by wet oxidation using cold 6% H\(_2\)PO\(_4\)/persulfate and infrared analysis of the resulting CO\(_2\) (Smith et al., 1981). Inorganic carbon was calculated as the difference between total carbon and organic carbon. Sediment surface area was measured by BET analysis of freeze-dried unamended samples by Omicron Technology Corp. (Berkeley Hgts., N.J.). Mineralogy was determined by X-ray diffraction analysis (Philips Norelco) using Ni-filtered Cu Ka radiation. The presence of metahalloysite is likely responsible for the relatively high surface area of KS sediment despite its coarse grain size as compared to CLB sediment.

**RESULTS AND DISCUSSION**

**Adsorption measurements**

Previous adsorption studies with aquatic sediments have relied, for the most part, on non-sterile samples to which relatively large amounts of nonlabelled xenobiotics have been added. Two factors make this approach inappropriate for experiments involving readily degraded short-chain organic intermediates which are typically found only at trace levels in natural sediments. First, as mentioned above, these latter experiments need to be conducted under sterile conditions due to the fast turnover rates of these compounds. Second, these experiments require the use of radio-labelled adsorbates because of the much lower concentrations of SCOAs in natural sediments as compared with the levels commonly used in xenobiotic studies.

The requirement for sterile experiments presents a major methodological obstacle due to the many potential physical and chemical effects associated with conventional sterilization techniques. We have found gamma-ray irradiation to be the most desirable method of sediment sterilization for the following reasons: a) it is highly effective in eliminating microbial SCOAs in sediment (Fig. 1); b) samples can be kept sealed in anaerobic glass jars during treatment; c) the radiation is not seriously affected by sample self-adsorption (McLaren, 1969); d) radioactivity is not induced in samples; and e) radiation-induced chemical changes are small compared to alternative methods (Saloni et al., 1967; McLaren, 1969), although it is possible that irradiation may have resulted in changes in the organic composition of the sediment that could affect our results.

**Adsorption kinetics**

The kinetics of OA adsorption was investigated by performing time-course experiments (Fig. 2). Samples

\[
S = (A \cdot B) - \left[ D \left( E f_w d^{-1} \right) - V \right]
\]  

where:

- \(S\) = dpm adsorbed
- \(A\) = dpm adsorbed/mass of sediment pellet subsample (g)
- \(B\) = sediment net weight post-centrifugation (g)/tube
- \(D\) = dpm dissolved/volume of supernatant (ml)
- \(E\) = pre-centrifugation sediment net weight (g)/tube
- \(f_w\) = fraction of water in the sediment (g/g)
- \(d\) = density of the liquid phase (porewater + added solutions) (g/ml)
- \(V\) = volume of supernatant (ml)/tube = \((B - E)/d\).
Sediment adsorption of organic acids

represented Means of triplicate samples (error bar indicates standard error; the standard errors of other stearate data points are smaller than the symbols).

were processed as described above, except that the first acetate and butyrate WB samples were not centrifuged, thereby allowing elapsed times of only 1 min.

Acetate adsorption onto CLB sediment did not significantly change after 20 min; other OA-sediment mixtures reached equilibrium in shorter time periods. These experiments showed that adsorption could be measured using short equilibration periods, thereby reducing the risks of errors due to accidental microbial contamination and the subsequent decomposition of the very labile SCOAs studied.

**Partition coefficients**

Figures 3–5 show the partition coefficients measured over large dissolved OA concentration ranges in the three sediments studied. In general, the coefficients displayed the following trends: stearate > acetate ≥ butyrate > lactate, and CLB > KS > WB. These results reflect 1) the polarities of the dissolved organic acids, and 2) the relatively nonpolar nature of the sand in the KS and WB sediments compared to the clays in the KS and CLB sediments. Dielectric constants provide a convenient means of estimating the polarity of molecules (e.g., Bell and Gross, 1929) when molecular dipole moment values are not available, as is the case for most organic acids. Table 2 compares our measured $K_d$ values with published dielectric constant data.

Greater OA polarity results in greater solubility in porewater, and, hence, lower adsorption onto solid surfaces. The presence of polar functional groups on the surfaces of clays (e.g., Kümmer and Stumm, 1980), and the relative lack of such groups on the surfaces of the carbonate sands, are likely to be a major factor controlling the sediment polarity. The result of these differences is the larger adsorption of the OAs onto CLB and, to a lesser degree, KS sediments as compared to WB sediments. This relationship, however, is likely to be complicated by the effects of organic coatings (see “Effect of organic coatings”, below).

The constancy of $K_d$ as a function of dissolved OA concentration indicates that the adsorption isotherms (mass adsorbed vs. dissolved concentration) are linear over the ranges used, thus suggesting that OA adsorption is not limited by the availability of surface adsorption sites in these sediments (Giles et al., 1974). The latter hypothesis can be tested by using the surface area data presented in Table 1 to estimate the concentration of SCOAs that would be needed to produce monolayer films on the different sediments: WB, 75 mmol m$^{-2}$; KS, 860 mmol m$^{-2}$; CLB, 190 mmol m$^{-2}$. These values are much larger than the concentrations used in the adsorption experiments, and are greater than 1000 times higher than the in situ CLB SCOA concentrations (Sansone, 1986). The hypothesis is further supported by the fact that the degree of adsorption by the three sediments is not correlated with the differences in their surface areas.
The partition coefficients measured for CLB and WB sediments may have been affected by the use of sediment slurries. Data of O'CONNOR and CONNOLLY (1980) and Di TOrO et al. (1985) indicate that for a variety of sorbates there may be up to a 1:1 inverse relationship in sediment slurry experiments between the partition coefficient measured and the particle concentration. Thus, the partition coefficients we report for CLB and WB sediments may be up to 1.3–1.8 and 1.1–1.3 times too high, respectively, for in situ conditions since the sediments were diluted by these amounts.

**Percent adsorption and SCOA bioavailability**

The percentage of the total sediment OA pools that are adsorbed onto the solid phase of the sediments studied are listed in Table 3. These results were calculated using the following relationship:

\[
P = \frac{R}{R + 1} \times 100\%
\]

where:

- \(P\) = percentage of total sediment OA adsorbed
- \(R = K_d P (1 - f_a) \rho^{-\lambda}\)
- \(\rho\) = density of the porewater (g/ml).

Stearate is nearly completely adsorbed, as would be expected from its very low polarity. Lactate, which is the most polar of the OAs studied, is not significantly adsorbed onto WB sediment. The significantly higher adsorption of lactate onto CLB sediment suggests that the presence of polar functional groups on the clay surfaces (e.g., KUMMERT and STUMM, 1980) may be important in controlling SCOA adsorption in this type of sediment.

Our results are consistent with those of SHAW et al. (1984); they reported that 10% to 40% of acetate added to Skan Bay sediments became associated with sediment particles. Since only a fraction of the acetate, butyrate, and lactate pools of the sediments studied are adsorbed onto the solid phase, it is likely that adsorption is at most a relatively minor control on the bioavailability of SCOAs. Nevertheless, other SCOA-sediment interactions such as clay-layer intercalation (FLETCHER et al., 1980; STOTZKY, 1980) may be important.

### Table 2. Dielectric constants for the organic acids studied (data from Weast, 1985), and the corresponding mean sediment partition coefficients. The dielectric constant of water is shown for comparison. ND = not determined.

<table>
<thead>
<tr>
<th>Organic acid</th>
<th>Partition coefficient (Kd)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CLB</td>
</tr>
<tr>
<td>Water</td>
<td>79</td>
</tr>
<tr>
<td>Lactate</td>
<td>22</td>
</tr>
<tr>
<td>Acetate</td>
<td>6.2</td>
</tr>
<tr>
<td>Butyrate</td>
<td>3.0</td>
</tr>
<tr>
<td>Stearate</td>
<td>2.3</td>
</tr>
</tbody>
</table>

### Table 3. Percent of total organic acid pools adsorbed onto sediment solid phase. The range of values measured is shown in parentheses. ND = not determined.

<table>
<thead>
<tr>
<th>Organic acid</th>
<th>Mean % adsorbed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CLB</td>
</tr>
<tr>
<td>Stearate</td>
<td>99 (98-100)</td>
</tr>
<tr>
<td>Acetate</td>
<td>24 (4-39)</td>
</tr>
<tr>
<td>Butyrate</td>
<td>24 (4-35)</td>
</tr>
<tr>
<td>Lactate</td>
<td>9 (0-18)</td>
</tr>
</tbody>
</table>
The potential effects of sediment dilution during our experiments (see "Partition coefficients", above) could result in overestimates of the calculated percent SCOAs adsorption (Table 3) by up to a factor of approximately 1.4 and 1.2, respectively, for CLB and WB sediments. Such an effect would further confirm our conclusion that only a limited amount of SCOAs adsorption occurs in these sediments.

**Effect of organic coatings**

For each of the OAs studied there was an analogous approximately linear relationship between the sediment organic matter content and $\log(K_d)$ (Fig. 6). Our results are similar to those reported by O'CONNOR and CONNOLLY (1980) for kepone, and support the hypothesis that OA adsorption is largely due to interaction of the OAs with organic coatings on the sediment solid phases. This hypothesis is further supported by the results of ZULLIG and MORSE (1983), who found no adsorption of butyrate from synthetic seawater onto clean calcium carbonate mineral surfaces. Further studies with other sediments will be needed, however, to determine whether the measurement of bulk organic content can be a useful aid in estimating OA adsorption onto natural sediments.

**CONCLUSIONS**

The methods presented here provide a means of studying the adsorption of extremely bioactive compounds onto natural sediments. The use of gamma-ray irradiation allows the study of compounds with very fast rates of biological turnover (SCOAs turnover rate constants can be larger than 10 h$^{-1}$ in organic-rich sediments, e.g., SANSONE, 1986). The use of natural sediments circumvents the uncertainties resulting from extrapolating results from experiments using clean mineral phases to the complicated surfaces of natural sediments.

The results of this study suggest that the adsorption of SCOAs onto marine sediments can be predicted by a knowledge of the polarity of these compounds and the characteristics of the surfaces of the sediment solid phase. Even in fine carbonate sand the availability of surface area does not appear to limit adsorption. Since the types of sediment used in this study covered a broad range, it is likely that the data presented here will be useful in predicting the behavior of SCOAs in other marine sediments. Nevertheless, further research with natural sediments will be needed to determine the effect of **in situ** conditions (e.g., temperature, redox state, and sediment organic content) on adsorption processes.

We conclude that only relatively small fractions of the total SCOAs pools are bound to the sediment solid phase, and thus adsorption is at most a relatively minor control on the bioavailability of SCOAs. Thus the observations of highly restricted bioavailability of acetate in marine sediments (e.g., CHRISTENSEN and BLACKBURN, 1982; SHAW et al., 1984; PARKES et al., 1984) may be largely due to other, currently unknown phenomena.

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**FIG. 6.** Measured partition coefficients (arithmetic means of data presented in Figs. 3–5) vs. the organic matter content (% dry weight) of the sediments (data from Table 1).


