Anionic Polysaccharide Sorption by Clay Minerals

Katerina M. Dontsova* and Jerry M. Bigham

ABSTRACT

An influence of clay mineral composition on C turnover in surface soils is widely assumed but poorly documented. The objective of this study was to evaluate the effect of various clay minerals on polysaccharide sorption under different environmental conditions, including pH, ionic strength, and cation type. Xanthan, an anionic polysaccharide produced by Xanthomonas campestris, was used to represent soil microbial exopolysaccharides. Highly significant effects (P > F < 0.0001) were observed for type of clay mineral, pH, xanthan concentration, and electrolyte concentration. Sorption decreased with increase in pH from 3 to 8, consistent with an increase in the negative charge of both the clay surface and xanthan molecules. The presence of 10 mmol L⁻¹ Ca(NO₃)₂ made sorption possible at pH values above the pKa of xanthan. Divalent cations (Sr²⁺, Ca²⁺, and Mg²⁺) enhanced sorption to a greater degree than monovalent cations (K⁺, Na⁺, and Li⁺) at the same ionic strength, indicating that cations participated in the binding of xanthan to clay surfaces. Generally, sorption was smallest with kaolinite and greatest with a low-charge (0.62 e layer charge per unit cell) smectite where layer charge originated mostly in the tetrahedral positions. Average sorption was two times greater for smectite than for kaolinite, indicating that clay mineral composition influenced polysaccharide sorption; however, contributions may not be significant on a field scale.

Surveys conducted in the central United States have commonly reported a positive correlation between organic C and soil clay content, e.g., Nichols (1984), Franzmeier (1988), and Konen et al. (2003). An influence of clay mineral composition on C turnover has also been speculated, but relationships have been difficult to verify because of the potential for multiple interactions among vegetation, landscape position, drainage, and soil chemistry.

A few researchers have compared organic matter (OM) properties and turnover in adjacent soils with different mineral composition (Arai et al., 1996; Parfitt et al., 2002) or in different particle-size fractions of a single soil (Gonzalez and Laird, 2003; Kahle et al., 2003), but the limited number of such comparisons has made firm conclusions about mineral–OM relationships difficult to achieve. Feller (1995) (as quoted in Feller and Beare, 1997) and Wattel-Koekkoek et al. (2001) analyzed large populations of soils in the tropics and found no difference in total soil OM (SOM) content between kaolinitic and smectitic soils. On the other hand, Wattel-Koekkoek et al. (2001) observed that kaolinitic materials were enriched with polysaccharides; whereas, smectite-associated OM contained more aromatic compounds.

Polysaccharides comprise about 10% of the OM in soils (Hayes and Swift, 1978; Cheshire, 1979) and are thought to play an essential role in the stabilization of soil structure (Tisdall and Oades, 1982; Robert and Chenu, 1992). Polysaccharides originate from both plants and microorganisms (Cheshire et al., 1979), but soil clay fractions are dominated by microbial rather than plant-derived polysaccharides (Feller and Beare, 1997). According to Foster (1981), microbial polysaccharides coat clay platelets, occupy crevices of submicron size within mineral aggregates, and bind clay particles together. Their position in small pores and their association with the clay fraction are believed to protect polysaccharides from degradation (Chenu and Stotzky, 2002).

Microbial polysaccharides are mostly net negatively charged compounds (Finch et al., 1967; Clapp and Emerson, 1972), particularly in neutral and alkaline environments because of an ionic acid component (Cheshire, 1979). Studies on the sorption of soil polysaccharides (Finch et al., 1967; Guckert et al., 1975) and anionic polysaccharides produced from laboratory cultures (Parfitt and Greenland, 1970; Clapp and Emerson, 1972; Parfitt, 1972; Labille et al., 2003) have largely been done using montmorillonite. Finch et al. (1967) showed that more polysaccharide was adsorbed by montmorillonite than kaolinite, and they attributed the difference to the greater surface area (SA) of the montmorillonite. Their comparison was not conducted under identical conditions, and it has been demonstrated that pH (Finch et al., 1967), exchangeable cations (Santoro and Stotzky, 1967; Parfitt and Greenland, 1970; Guckert et al., 1975), and electrolytes (Labille et al., 2003) can also affect the sorption of anionic polysaccharides.

In general, the published literature does not provide a complete picture of the effects of clay mineral composition on the accumulation of SOM, and there is a need for systematic studies under controlled laboratory conditions using defined organic substances and well-characterized clay minerals to resolve important chemical and mineralogical factors affecting retention of SOM. Therefore, the objective of this study was to evaluate the effect of clay mineral composition on the sorption of an anionic polysaccharide, representing one of the components of SOM, under different pH, electrolyte, and cation conditions typical of soil environments.
Xanthan was used as a model for microbial exopolysaccharides in this study. It is a naturally occurring, large-molecular-mass anionic polysaccharide produced by Xanthomonas campestris. Xanthan contains D-glucose, D-mannose, and D-gluconic acid in the molar ratio 2:2:1 (Sutherland, 1994), resulting in one COOH group per unit. The primary structure of xanthan is a cellulose chain, in which trisaccharide side chains of two mannoses and one gluconic acid are attached to every other D-glucosyl residue. It can also carry O-acetyl groups on the C6 position of the internal α-D-mannosyl residue and pyruvate ketal on the side-chain-terminal β-D-mannosyl residue, which would add another COOH group. About 60% of the terminal mannose residues are 4,6-pyruvated, and the inner mannose is mostly 6-acetylated (Fig. 1). The molecular mass of xanthan varies between 0.9 and 1.6 × 10^6 Da (Sutherland, 1994).

Xanthan readily dissolves in water and forms viscous solutions that are stable in the presence of common inorganic salts. Similar to most microbial exopolysaccharides, xanthan is generally considered to adopt a double-helical conformation when in solution at room temperature (Sutherland, 1994), and it forms strands or a network of fibers when dried (Chenu, 1993). The xanthan used in this study was purchased as a K salt from Sigma Chemical Co. (Catalog no. G-1253, Sigma-Aldrich, St. Louis, MO). A stock solution was prepared fresh before each experiment by dissolving the dried powder in water or an electrolyte solution overnight.

### Clay Minerals

Specimen clay minerals (van Olphen and Fripiat, 1979) were obtained from The Clay Minerals Society Source Clays Repository (Purdue Univ., Dep. of Agron.). The samples represented a range of properties consistent with the mineralogical diversity of soils in the central United States (Table 1). The clays were fractionated by sedimentation using an automatic fractionator following pretreatment with 1 mol L\(^{-1}\) Na acetate buffer at pH 5 to remove carbonates, 30% (w/w) H\(_2\)O\(_2\) to remove OM, and 0.25 mol L\(^{-1}\) NaClO to achieve dispersion with sonication. The fractionated clays (<2 μm) were exchanged with Ca and washed free of excess salt by centrifugation. The clays were exchanged with Ca because it is the dominant exchangeable cation in most Midwestern soils. After freeze drying, the <2 μm materials were analyzed for both external (Brunauer–Emmett–Teller [BET] N\(_2\)) and total (ethylene glycol monoethyl ether [EGME]) SA. In addition, the cation exchange capacity (CEC) at pH 7 was determined using Ca as the index cation. In this process, the clays were expanded with NaCl, then saturated with CaCl\(_2\), and washed with deionized (DI) water to remove excess salt. The exchangeable Ca was then displaced with Mg, and the leachate was analyzed for Ca.

### Adsorption Experiments

Adsorption experiments were conducted to assess the effects of polysaccharide concentration, pH, electrolyte concentration, and cation type on sorption of xanthan by different clay minerals. Subsamples of the clays (0.15 g) were ultrasonically dispersed in water or salt solution, adjusted to the desired pH using 0.1 mol L\(^{-1}\) HNO\(_3\) or saturated (less than 0.025 mol L\(^{-1}\)) Ca(OH)\(_2\) solutions, and mixed with the appropriate xanthan solution to form 40 mL of a final suspension with 3.75 g L\(^{-1}\) of clay. Preliminary experiments and literature reports (Wen, 2002) showed that the amount of xanthan adsorbed was proportional to the quantity of clay; therefore, the same amount of clay was used in all experiments. After 12-h equilibration on a reciprocal shaker (100 rpm) at room temperature (18°C), the clay–xanthan suspensions were centrifuged for 30 min at 6328 × g, and total organic C (TOC) in the supernatant was measured using a Rosemount external (Brunauer–Emmett–Teller [BET] N\(_2\)) and total (ethylene glycol monoethyl ether [EGME]) SA. In addition, the cation exchange capacity (CEC) at pH 7 was determined using Ca as the index cation. In this process, the clays were expanded with NaCl, then saturated with CaCl\(_2\), and washed with deionized (DI) water to remove excess salt. The exchangeable Ca was then displaced with Mg, and the leachate was analyzed for Ca.

### Table 1. Properties of the standard clay minerals used in this study (van Olphen and Fripiat, 1979).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mineral</th>
<th>CEC† cmol kg(^{-1})</th>
<th>EGME SA‡ m(^2) g(^{-1})</th>
<th>N(_2) SA§ m(^2) g(^{-1})</th>
<th>Tet.</th>
<th>Oct.</th>
<th>Total</th>
<th>% Oct.</th>
</tr>
</thead>
<tbody>
<tr>
<td>KGa-1</td>
<td>Kaolinite</td>
<td>2 ± 0#</td>
<td>44 ± 26</td>
<td>13 ± 0</td>
<td>−0.16</td>
<td>−0.52</td>
<td>−0.68</td>
<td>76</td>
</tr>
<tr>
<td>DM-1</td>
<td>Illite</td>
<td>26 ± 1</td>
<td>183 ± 33</td>
<td>53 ± 1</td>
<td>0.00</td>
<td>−0.62</td>
<td>−0.62</td>
<td>100</td>
</tr>
<tr>
<td>SW-1</td>
<td>Na mont.††</td>
<td>78 ± 2</td>
<td>757 ± 33</td>
<td>15 ± 6</td>
<td>−0.04</td>
<td>−1.00</td>
<td>−1.14</td>
<td>88</td>
</tr>
<tr>
<td>SHCa-1</td>
<td>Hectorite</td>
<td>89 ± 3</td>
<td>828 ± 56</td>
<td>92 ± 7</td>
<td>0.10</td>
<td>−1.08</td>
<td>−1.18</td>
<td>92</td>
</tr>
<tr>
<td>NG-1</td>
<td>Nontronite</td>
<td>91 ± 5</td>
<td>675 ± 75</td>
<td>69 ± 1</td>
<td>−0.14</td>
<td>−1.00</td>
<td>−1.14</td>
<td>88</td>
</tr>
<tr>
<td>SA-1</td>
<td>Ca mont.</td>
<td>121 ± 2</td>
<td>844 ± 55</td>
<td>80 ± 4</td>
<td>−0.10</td>
<td>−1.08</td>
<td>−1.18</td>
<td>92</td>
</tr>
<tr>
<td>Sca-2</td>
<td>Otay mont.</td>
<td>122 ± 3</td>
<td>844 ± 46</td>
<td>91 ± 3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

† CEC = cation exchange capacity at pH 7 measured by exchange of Mg for Ca.
‡ EGME SA = total surface area by ethylene glycol monoethyl ether method.
§ N\(_2\) SA = external surface area after heating to 105°C overnight.
# Standard deviation.
†† mont., montmorillonite.
in excess of the time needed to reach equilibrium, which has been reported to be less than 1 h (Moavad et al., 1974; Guckert et al., 1975; Wen, 2002). The quantity of xanthan adsorbed was determined by difference between the concentration of TOC in the supernatant liquid of samples with and without clay. Control measurements (without clay) showed the C content of xanthan in the supernatant to vary between 42% without electrolyte and 31% in the presence of electrolyte. These values were less than calculated from the molecular formula (43%), probably as a result of the formation of some gel-like structures that sedimented during centrifugation (Sutherland, 1994). Any change in xanthan concentration caused by dissolved salt was corrected by using a control (no clay added) for each treatment. The pH of the supernatant was measured (Orion 420A Benchtop pH Meter, Thermo Electron Corp., Waltham, MA) immediately after TOC was determined.

Xanthan sorption isotherms for all specimen clays were obtained at pH 4 in suspensions with and without electrolyte [10 mmol L$^{-1}$ Ca(NO$_3$)$_2$]. Xanthan concentrations ranged between 0 and 200 mg L$^{-1}$ with a 25 mg L$^{-1}$ step interval.

To study the effect of pH on sorption of xanthan, three clays with different charge characteristics (SAz-1, SWy-1, and KGa-1) were equilibrated with 100 mg L$^{-1}$ xanthan solutions with and without electrolyte [10 mmol L$^{-1}$ Ca(NO$_3$)$_2$]. The pH range was 3 to 8 with a 0.5-pH step interval.

The effect of electrolytes on sorption was evaluated for all clays by equilibrating them with 100 mg L$^{-1}$ xanthan solutions in 0, 1, 2.5, 5, 7.5, and 10 mmol L$^{-1}$ Ca(NO$_3$)$_2$ under two pH regimes, 4 and 7, representing acid and neutral conditions. Concentrations of electrolyte were within the range previously observed for saturation extracts from common soils in the central USA (Dontsova and Norton, 2002).

To study the effect of cation type on the sorption of xanthan, samples of SAz-1 were washed with nitrate salts of Li$^+$, Na$^+$, K$^+$ (1 mol L$^{-1}$), Mg$^{2+}$, Ca$^{2+}$, Sr$^{2+}$ (0.5 mol L$^{-1}$), and Al$^{3+}$ (0.33 mol L$^{-1}$) three times, and excess salt was removed by multiple centrifugations with DI water. The samples were then equilibrated with 100 mg L$^{-1}$ solutions of xanthan with salt concentrations ranging between 0 and 20 mmol L$^{-1}$.

**RESULTS AND DISCUSSION**

**Xanthan Concentration**

The isotherms obtained as functions of xanthan concentration were L-shaped (Giles et al., 1974), as previously observed for soil polysaccharides (Finch et al., 1967). When concentrations of xanthan were increased from 0 to 200 mg L$^{-1}$ at pH 4, a stepwise increase in adsorption was observed for most clay minerals (Fig. 2). In the presence of 10 mmol L$^{-1}$ Ca(NO$_3$)$_2$, kaolinite was the only mineral that reached a single apparent plateau in the concentration range studied. Without background electrolyte, the same tendency for multistep adsorption was observed, but the steps were not as well defined. Moreover, the first plateau in adsorption with electrolyte was generally achieved at lower equilibrium concentrations of xanthan than without electrolyte (approximately 15 and 25 mg L$^{-1}$, respectively). The effect of background electrolyte indicated a strong interaction between xanthan molecules and Ca ions, possibly suggesting precipitation of xanthan at mineral surfaces rather than adsorption (sensu strictu), as the term is used in this and other reports.

Stepwise adsorption behavior suggests the formation of multiple layers of polysaccharide on the clay surface and is reportedly characteristic of xanthan (Malik and Letey, 1991) and other anionic polysaccharides (Finch et al., 1967; Guckert et al., 1975). The formation of multiple layers may result in the adsorption of xanthan in quantities that exceed the available SA of the clay (Olness and Clapp, 1973; Parfitt and Greenland, 1970; Moavad et al., 1974); however, the rigid structure of xanthan makes calculation of surface coverage difficult. Whereas simple, uncharged sugars assume a flat configuration with adsorption on montmorillonite (Greenland, 1956), xanthan tends to retain its helical tertiary structure (Chenu et al., 1987). This structure results in an uncharged core ringed with charged groups that can enter into reactions with other compounds in solution or with charged sites on the clay surface by bridging with multivalent cations.

The values obtained for xanthan sorption on smectites in this study were in reasonable agreement with previous reports. Sorption by Ca-exchanged SWy-1 was about 2 g kg$^{-1}$ TOC (5 g kg$^{-1}$ xanthan) under neutral conditions from a 100 mg L$^{-1}$ xanthan solution in 1 mmol L$^{-1}$ Ca(NO$_3$)$_2$, and 9 g kg$^{-1}$ TOC (22.5 g kg$^{-1}$ xanthan) from a 200 mg L$^{-1}$ xanthan solution in 10 mmol L$^{-1}$ CaCl$_2$. Clapp and Emerson (1972) reported the adsorption of 4.8 g kg$^{-1}$ of xanthan from a 50 mg L$^{-1}$ solution and 27.8 g kg$^{-1}$ from a 250 mg L$^{-1}$ solution by Ca montmorillonite with a background of <1 mmol L$^{-1}$ CaCl$_2$. Reported results for other anionic polysaccharides vary between 20 and 30 g kg$^{-1}$ for Na montmorillonite (Finch et al., 1967; Labille et al., 2003), 90 to 150 g kg$^{-1}$ for H montmorillonite (Finch et al., 1967), and up to 115 g kg$^{-1}$ for Ca montmorillonite (Labille et al., 2003). The reported values depended on experimental conditions, and conditions varied between experiments.

Although the amounts of polysaccharide sorbed in the current study were small, they would probably contribute to the stabilization of soil structure. Clapp and Emerson (1972) showed that the adsorption of as little as 1 to 2 g kg$^{-1}$ of xanthan was enough to prevent dispersion of montmorillonite. In other studies, maximum aggregate stability was achieved at 10 g kg$^{-1}$ for neutral polysaccharides (Chenu et al., 1987) and 20 g kg$^{-1}$ for anionic polysaccharides (Labille et al., 2003).

**Electrolyte Concentration**

Greater adsorption of xanthan was observed in the presence than in the absence of 10 mmol L$^{-1}$ Ca(NO$_3$)$_2$ (Fig. 2). At pH 4, there was a 2.3- to 6.5-fold increase in adsorption with electrolyte (Table 2), and this increase was significant at the 0.05 probability level for all clays. At pH 7, the relative increase in adsorption of xanthan in the presence of Ca(NO$_3$)$_2$ was also significant and even greater than at pH 4 (4.5- to 141.5-fold). The positive response to electrolyte agrees with the one described for anionic polymers by Theng (1982), who attributed the effect to screening of the charge on the polyanion with a resulting decrease in electrostatic repulsion between surfaces.

A systematic increase in the concentration of Ca(NO$_3$)$_2$ from 0 to 10 mmol L$^{-1}$ resulted in an increase in adsorp-
Fig. 2. Sorption of total organic C (TOC) by sample clays (see Table 1) at room temperature (18°C) as a function of the concentration of xanthan at pH 4, both in the (a) presence and (b) absence of 10 mmol L\(^{-1}\) Ca(NO\(_3\))\(_2\). Values are averages of 1 to 10 replications. Error bars are standard deviations of the means.

The sorption of xanthan for all clays, approaching a plateau in the upper concentration range (Fig. 3). The increase was greater for low-charge smectites than for high-charge smectites and illite, which had about the same range as kaolinite at neutral pH but were greater than kaolinite at acid pH. At pH 4, a plateau was reached for the low-charge smectites but not the high-charge ones. With 10 mmol L\(^{-1}\) Ca(NO\(_3\))\(_2\), there was at least twice as much positive charge available in solution (10.36 mmol L\(^{-1}\)) as there were negatively charged sites on clay surfaces and xanthan molecules (3.79 mmol L\(^{-1}\)); therefore, a plateau would be expected.

Guckert et al. (1975) reported that the sorption of soil polysaccharides by smectite SAz-1 increased with an increase in background electrolyte, but kaolinite showed little difference as a function of electrolyte concentration. This result was attributed to the small CEC of kaolinite and the absence of charge on its planar surfaces. A similar difference in behavior between smectite and kaolinite was not observed in the current study.
Table 2. Effect of Ca(NO₃)₂ concentration, pH, and clay properties on sorption total organic C by clay minerals at 100 mg L⁻¹ concentration of xanthan.

<table>
<thead>
<tr>
<th>Clay</th>
<th>pH 4 0 mmol L⁻¹</th>
<th>pH 4 10 mmol L⁻¹</th>
<th>pH 7 0 mmol L⁻¹</th>
<th>pH 7 10 mmol L⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>IMt-1</td>
<td>2.35 AB h‡</td>
<td>5.49 BC a</td>
<td>0.32 A c</td>
<td>2.12 C b</td>
</tr>
<tr>
<td>KGa-1</td>
<td>1.31 B h‡</td>
<td>3.90 C a</td>
<td>0.72 A b</td>
<td>3.23 BC a</td>
</tr>
<tr>
<td>NG-1</td>
<td>3.25 A h‡</td>
<td>7.95 A a</td>
<td>0.14 A e</td>
<td>6.46 A a</td>
</tr>
<tr>
<td>SAz-1</td>
<td>1.31 B c‡</td>
<td>6.03 B a</td>
<td>0.02 A d</td>
<td>2.83 BC b</td>
</tr>
<tr>
<td>SCa-2</td>
<td>0.87 B c‡</td>
<td>5.22 BC a</td>
<td>0.06 A e</td>
<td>3.72 BC b</td>
</tr>
<tr>
<td>SHCa-1</td>
<td>1.64 B h‡</td>
<td>5.19 BC a</td>
<td>0.52 A b</td>
<td>4.95 AB a</td>
</tr>
<tr>
<td>SWy-1</td>
<td>1.08 B c‡</td>
<td>7.03 AB a</td>
<td>0.21 A e</td>
<td>4.23 B b</td>
</tr>
</tbody>
</table>

† Numbers followed by the same letter are not significantly different at 0.05 probability level. Uppercase letters are for comparison between clays within pH and Ca(NO₃)₂ treatments. Lowercase letters are for comparison between treatments within the clay.

Although sorption at elevated concentrations of electrolyte at low pH was greater for smectites, the relative increase did not depend on layer charge.

**Electrolyte Type**

Sorption of xanthan by smectite SAz-1 from 100 mg L⁻¹ solutions using nitrate salts of various monovalent (K⁺, Na⁺, and Li⁺) and divalent (Sr²⁺, Ca²⁺, and Mg²⁺) cations as background electrolyte showed that an increase in ionic strength from 0 to 30 mmol L⁻¹ led to an increase in adsorption, approaching a plateau in the upper concentration range (Fig. 4a). This behavior was similar to that observed previously for Ca²⁺. Divalent cations enhanced adsorption to a greater degree than monovalent cations at the same ionic strength.

The data were also plotted as a function of cationic strength (Fig. 4b) because this parameter should provide a better measure of the ability of cations to neutralize negative charge on clay. The following formula describes ionic strength:

\[
I = \frac{1}{2} \sum z^i C_i
\]

where \( C \) is the concentration of each ion present in solution and \( z \) is its charge. Cationic strength, \( I_c \), is defined in this paper as a product of cation concentration, \( C_c \), and its squared charge, \( z_c^2 \):

\[
I_c = z_c^2 C_c
\]

Despite the fact that at the same cationic strength, there are more unit charges in monovalent than in divalent cation solutions, sorption was greater in the divalent system. This result indicated that charge screening and compression of the double layer did not entirely explain the electrolyte effect observed in our study and supported active participation by cations in xanthan binding. McBride and Baveye (2002) stated that cations provide an attractive force between negatively charged colloidal particles because they are electrostatically attracted to both surfaces. Cation bridging has also been used to explain the sorption of negatively charged sugars by montmorillonite (Parfitt, 1972; Labille et al., 2003), and this mechanism was supported by spectroscopic evidence of associations between exchangeable cations and carboxylic groups of the polysaccharides (Parfitt, 1972).

Previous research has shown a decrease in sorption of anionic polymers with an increase in cation size and electronegativity for monovalent cations (Mortensen, 1962; Theng and Scharpenseel, 1975) and an increase in sorption with a decrease in cation size for multivalent cations (Mortensen, 1962; Theng and Scharpenseel, 1975; Theng, 1976). This behavior indicated that anionic polymers can remove water from monovalent cations and bind directly to the exchangeable cation, whereas with divalent cations, binding occurs through the water of hydration. The current study did not show differences between divalent cations of different size, but it did indicate a difference between more hydrated Li⁺ and less hydrated K⁺.

Aluminum caused flocculation of both the clay and xanthan at the minimum concentration used (0.3 mmol L⁻¹), making sorption measurements impossible. This behavior agreed with observations of Sutherland (1994), who noted that in the presence of trivalent metal ions, xanthan solutions became cross-linked to form gels.

**pH**

Total sorption of xanthan was greater at pH 4 than at pH 7 for all clays (Table 2). A 1.1- to 2.6-fold difference in sorption was observed between pH 4 and 7 in 10 mmol L⁻¹ Ca(NO₃)₂. This difference was significant at the 0.05 probability level for IMt-1, SAz-1, SCa-2, and SWy-1 (2.6, 2.1, 1.4, and 1.7 times increase, respectively) and not significant for KGa-1, NG-1, and SHCa-1 (1.2, 1.2, and 1.1 times increase). Such behavior was consistent with an increase in the negative charge of both xanthan and clay as the pH increased and variable charge sites dissociated. Finch et al. (1967) showed that a decrease in pH from 7 to 4.4 reduced the electrophoretic mobility of soil polysaccharides by a factor of about 10.

Xanthan sorption was studied in more detail for SAz-1, KGa-1, and SWy-1 over a pH range of 3 to 8. As before, sorption decreased with increase in pH (Fig. 5). Without electrolyte, xanthan sorption was small, approximately 1 g kg⁻¹ TOC for all three clays, and sorption increased only at pH values below 4. This behavior was similar to previous observations for polygalacturonic acid, which was not adsorbed by montmorillonite when the pH was 6 and above (Parfitt and Greenland, 1970). Low-charged smectite, SWy-1, displayed greater sorptive capacity at pHs < 4.0 than high-charged smectite, SAz-1, and kaolinite (Fig. 5). Burchill et al. (1981) noted increased sorp-
The presence of electrolyte allowed sorption to occur at circumneutral pH values; however, sorption still decreased with increase in pH. When straight lines were fitted to the data (Fig. 5), they showed that the decrease in sorption with increasing pH became more significant as layer charge increased in the order: KGa-1 < SWy-1 < SAz-1. Sample SAz-1 also showed a decline in sorption with a decrease in pH below 4, which was not observed for the other clays. According to Harter (1977), maximum adsorption usually occurs within one unit of the pKa for an organic compound. The dissociation constant for xanthan is between pH 3.2 and 4.1 (Young et al., 1994) and 4.5 and 5.5 (Welch, 1999) and may account for the observed sorption maximum.

**Mineral Composition**

A highly significant effect ($P > F < 0.0001$) of clay mineral type on xanthan sorption was observed (Table 2). It can be concluded from Fig. 2 and 3 and Table 2 that at pH 4.0 and 10 mmol L$^{-1}$ Ca concentration, sorption was smallest with kaolinite and greatest with NG-1, a low-

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**Fig. 3.** Adsorption of total organic C (TOC) by sample clays (see Table 1) from 100 mg L$^{-1}$ solutions of xanthan at room temperature (18°C) as a function of Ca(NO$_3$)$_2$ concentration at pH (a) 4 and (b) 7. Values are averages of 1 to 10 replications. Error bars are standard deviations of the means.
charge smectite where layer charge originates mostly in the tetrahedral positions. The increase in average sorption from kaolinite to smectite was by a factor of two. At pH 7.0 without electrolyte, low-charge smectites continued to have the greatest sorption, whereas high-charge smectites adsorbed similar amounts or even less than kaolinite. Under all the environmental conditions studied, illite (IMt-1) behaved similar to the high-charge smectite, SAz-1, despite differences in total layer charge, CEC, and total and external SA. This similarity may be explained by weathering of external surfaces of the illite particles, resulting in a smaller charge density on these surfaces.

To quantitatively evaluate the effect of clay properties on xanthan sorption, a series of linear regressions was performed. The retention of TOC by sediments has been previously linked to the EGME SA of smectites (Kennedy et al., 2002), the N₂ SA of clay fractions (Ransom et al., 1998; Adams and Bustin, 2001), and SA as measured by para-nitrophenol adsorption (Saggar et al., 1996, 1999). Intercalation has been observed for neutral polysaccharides in montmorillonite (Olness and Clapp, 1973) but not for anionic polysaccharides (Parfitt and Greenland, 1970). Therefore, external SA, as measured by N₂ sorption, should be a more important property in determining xanthan sorption than total SA.

Guckert et al. (1975) observed that the extent of polysaccharide sorption on montmorillonite was related to the exchangeable cation but not the SA. In the current study, we also observed no statistically significant relation between the sorption of xanthan from 100 mg L⁻¹ solutions and the N₂ SA, EGME SA, or CEC of the minerals studied. The only exception was a negative correlation between sorption at pH 7 without background electrolyte and CEC (\( P > F = 0.0288 \)). In general, sorption of xanthan without electrolyte was negatively correlated with N₂ SA, EGME SA, and CEC; whereas, the correlation was positive in the presence of background electrolyte. When sorption values were calculated on the basis of external SA (N₂ SA [\( \mu g \ m^{-2} \])), then the relationship between sorption and CEC became negative both with and without electrolyte and was significant for samples...
hedral charge significantly enhanced sorption (Fig. 6c), indicating that layer charge perhaps had a dual effect. Negative charge of the particles caused repulsion of the anionic xanthan, but it also facilitated sorption through cationic bridging, particularly in the presence of background electrolyte. Because tetrahedral charge tends to form stronger bonds with cations and is easier to neutralize than octahedral charge, it promotes sorption to a greater degree (Harter, 1977).

Steric considerations, i.e., a match between charge density on the clay and size of the organic molecule and its charge distribution, also affect sorption (Harter, 1977). Finch et al. (1967) observed preferential adsorption of the medium-charge (one uronic acid per six sugar residues) component from a mixture of soil polysaccharides. In this study, low-charge smectites apparently had a better match for the xanthan charge distribution than high-charge clays. Although correlations involving charge distribution used a limited number of samples and should be viewed with caution, the relationships were statistically significant. Anion exchange capacity (AEC) and the CEC/AEC ratio may also affect sorption (Stotzky, 1986); however, a lack of information on AEC in the current study did not permit an evaluation of this factor.

**CONCLUSIONS**

The sorption capacity of the minerals examined in this study depended on environmental conditions, including pH and the type and concentration of cations in the surrounding medium. Sorption generally was the greatest at low pH and electrolyte concentrations typical of field conditions. Although agricultural soils are usually limed, low pH can be expected locally in the rhizosphere as the result of root exudates containing organic acids. As extracellular polysaccharides are also concentrated in this zone, favorable conditions for polysaccharide sorption probably occur.

The sorption of xanthan was related to inherent properties of the studied clay minerals, such as N2 SA, CEC, and the amount of octahedral and tetrahedral charge. Negative correlations between sorption and CEC and octahedral charge indicated repulsion between negatively charged clay particles and the anionic xanthan molecules. Positive correlations between xanthan sorption and CEC and octahedral charge indicated repulsion between negatively charged clay particles and the anionic xanthan molecules. Positive correlations between xanthan sorption and the amount of tetrahedral charge indicated that the mechanisms of sorption probably involved cation bridging between surface-charge sites on the clays and the polysaccharide molecules. Overall, low-charge smectites sorbed the greatest amount of xanthan, and kaolinite the least, with high-charge smectites having intermediate sorption values. Illite behaved like high-charge smectite.

A highly significant effect ($P > F < 0.0001$) of clay type was observed on the sorption of xanthan. Differences between minerals accounted for a two- to threefold difference in sorption, indicating that soil mineral composition may be important in determining the quantity of polysaccharide stored in the soil, its turnover time, and its flux to the atmosphere. However, the effect of clay mineral composition was not as pronounced as might be expected from the wide range of properties represented.
Under field conditions where different minerals usually are present in mixtures, it should be expected that an effect of clay mineral composition on sorption of anionic polysaccharides will be less evident.

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