A Thesis presented by Sonya Boguslavsky to The Graduate School In Partial Fulfillment of the Requirements For the Degree of Master of Science in Earth and Space Sciences State University of New York At Stony Brook May, 2000

TABLE OF CONTENTS

Abstract
Acknowledgments
Introduction

Chapter 1. Methods
Samples
Analytical methods
  Cation exchange capacity
  Separation of the coatings
  pH measurement
  X-ray powder diffraction (XRD)
  Transmission electron microscopy (TEM)
  Scanning electron microscopy (SEM)
  Sorption of hydrophobic organic compounds
  Surface area measurements
  Total organic carbon (TOC)

Chapter 2. Cation exchange capacity
Results
Actual and potential acidity
Discussion

Figures
  Figure 1. Cation exchange capacity (CEC) of the core from Cathedral Pine County Park
Chapter 2. Cation exchange capacity of the sediments from Port Jefferson (sample 1), South Setauket (samples 6 and 7), Soil near Fox Pond and the beach cliff at David Weld Preserve

Tables (All tables for Chapter 2 are on a separate web page. This file is about 190 kb.)

Table 1. Cation exchange capacity of the different types of material

Table 2. Results of the measurement of cation exchange capacity

Table 3. Cation exchange capacity of the sediments from Port Jefferson, South Setauket, David Weld Preserve, Fox pond and Cathedral Pine County Park

Table 4. Relative ion concentration to the total cation exchange capacity

Table 5. pH values (BaCl₂ and pH)

Table 6. Concentration of hydrogen ion in the core from Cathedral Pine County Park

Chapter 3. Sorption of hydrophobic organic compounds

Introduction

Approach

Results

Discussion

Conclusions

Figures

Figure 1 (A-D). The comparison among whole sand Kd, coatings Kd, naked sand Kd, sonicated sand Kd but without separation of coatings, Kd HCl treated sand and the sum of coatings Kd * fraction of coatings and Kd of naked sand * fraction of naked sand

Figure 2. Correlation between the fraction of total organic carbon and Kd of the coatings. Coarse sand from Port Jefferson (samples 1 and 5) and coarse-medium sand from South Setauket (samples 6 and 7)

Figure 3. Correlation between surface area and Kd of the coated sand, coarse sand from Port Jefferson (samples 1 and 5) and coarse-medium sand from South Setauket (samples 6 and 7)

Tables (All tables for Chapter 3 are on a separate web page. This file is about 75 kb.)

Table 1. The Kd values for the whole sand, the coatings, the naked sand, the sonicated sand without separation of coatings and the sand without iron compounds

Table 2. Fraction of the coatings to the whole coated sand mass

Table 3. The estimation of the contribution of the naked sand and the coatings to the sorption of the whole sand

Table 4. Fraction of organic carbon
Table 5. Surface area

Table 6. The comparison among the log Koc whole sand, log Koc coatings, log Koc naked sand and predicted log Koc

Table 7. The comparison between experimental and predicted Ksa

Chapter 4. Composition of the coatings

Results

X-ray diffraction (XRD)
Scanning electron microscopy (SEM)
Transmission electron microscopy (TEM)
Total organic carbon (TOC)

Discussion

Figures

Figures 1 through 13 are not yet available.

Figure 1. XRD patterns of the air-dried fraction < 2 mm. Fine sand from beach cliff at David Weld Preserve (sample 10)

Figure 2 (A-B). The XRD patterns of 6M HCl treated and 300 °C heated sample 10

Figure 3. 2000 x SEM image. Coated mineral surface.

Figure 4. 2000 x SEM image. Coated mineral surface

Figure 5. 2000 x SEM image of the grains of the coarse heavily coated sand from Port Jefferson (sample 1)

Figure 6. 1000 x SEM image. Small particles of clay are on the surface of the large grain

Figure 7. 1000 x SEM image. Surface of the sample 1 (coarse sand)

Figure 8. 2000 x SEM image. Clear grain surface shows etch pits.

Figure 9. 1000 x SEM image Surface of the medium- coarse sand from Port Jefferson

Figure 10. 2000 x SEM. Surface of the coarse sand from Port Jefferson.
Cation exchange capacity (CEC) of glacial sand from different locations on Long Island was analyzed, using 0.1 M BaCl₂ extraction. The glacial sand consists of primarily quartz. Most quartz grains contain coatings on the surface. The CEC of sand analyzed in this study varies from 0.85 meq/100g for coarse sand-gravel to 21.3
meq/100g for fine sand. The CEC of sediments is function of grain size, mineralogy, amount of organic matter and amount of coatings on the grains. In this study grain size seems to be the most important factor in determining CEC. The distribution of exchangeable cations with depth was observed in the core 0-480 cm below the surface. The main exchangeable cation in 0-120 cm below the surface is Al (75-82% of the total CEC), at the depth 150 cm exchangeable Al contains < 2% of the total CEC. The fraction of exchangeable Na generally increases with depth from 10% of total CEC at 0-60 cm to 78% of total CEC at 420-440 cm. In the upper part of the sequence exchangeable Ca occupied 8% of the total CEC and below 90 its fraction is negligible. The distilled water and BaCl$_2$ pH was measured in the core. At 90-120 cm below the surface the BaCl$_2$ pH is lower than water pH, but below 120 cm water pH is lower than BaCl$_2$ pH. The CEC of untreated sand, naked sand and coatings was measured. In this sample coatings contribute 87% of the CEC. The fraction of the coatings in these samples varies from 0.8% to 13%.

Composition of these coatings were analyzed by using scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray diffraction (XRD). Total organic carbon (TOC) was measured on the sand and coatings. Results suggest that coatings composed of clay minerals (illite, kaolinite and chlorite) with minor amount of organic matter and iron compounds. Fraction of organic (foc) carbon on sand varies from 0.0002 to 0.00027. The foc on the coatings varies in the range from 0.0021 to 0.0076.

Results of short term hydrophobic organic compound sorption experiment suggest that the Kd (hexachlorobenzene) (HCB) for glacial sand varies from 2.5 ml/g to 10.7 ml/g. The Kd for coatings lies between 396 ml/g and 1480 ml/g. The Kd for naked sand is always lower than that observed for untreated sand and coatings varies between 1.55 ml/g and 9.02 ml/g. The coatings appear to be the main sorbent for HCB, 72.8 - 85 % of HCB sorbed on the coatings. Sonication of the sand increases Kd by 20.1-73.1 %. Sorption of HCB by the coatings is consistent with the amount of organic matter onto the coatings. The partitioning of HCB into coatings organic matter is likely control sorption. Some amount of organic matter remains unavailable for sorption of HOC. The results of this study suggest that in cation exchange and hydrophobic organic compound sorption the coatings play the major role.

I would like to thank my advisor Gill Hanson for his support, encouragement, for proofreading of hundreds of thesis drafts, and helping me throughout my research project. I thank Rich Reeder for teaching me microscopy techniques and his incredible patience with me. I thank Bruce Brownawell for introducing me to the world of organic geochemistry. I would also like to thank Martin Schoonen and Scott McLennan for their helpful advices. I am extremely grateful to the isotope lab people including: Mona Becker, Troy Rasbury, Joel Hurowitz, Andy Winslow, and Peter Schumann. Others in Stony Brook who have provided help and support Karen Baird, Melissa Nugent, Alessandro Dondollini.

I am grateful to office staff members Barbara Siemson, Iris Roth, Ann Cox and Jim Broyles. I would like to also thank Lee Ferguson for teaching me lab organic geochemistry techniques; David Hirschberg for analyzing samples for TOC and Ron Paulsen for providing samples. I am extremely grateful to my friend Peter for correcting my English and practicing the talks with me. And the Special thanks go to my family: my parents, my sister, my son and my husband.
Introduction

The objectives of this study are to:

1) determine the cation exchange capacity and sorption distribution coefficient of hydrophobic organic compounds for Long Island glacial sediments and

2) evaluate the importance of sediment coatings on the cation exchange and sorption capacity of sediments.

Ground water is the sole source of drinking water on Long Island. Thus it is important to understand how cations and near surface contaminants in aqueous solution may interact with sediments in the unsaturated zone as they infiltrate downward to the ground water. The transport of cations (e.g. metal ions, and ammonium ion), and hydrophobic organic compounds in aqueous solution through sediments is affected by sorption to sediments (Holmen and Gschwend, 1997; Coston et al, 1995; Wood et al, 1990; Ryan and Gschwend, 1992). As a result the elements or compounds may be retarded. Also ions in solution may exchange with ions sorbed onto sediments freeing the sorbed ions (Appelo and Postma, 1993, Stumm and Morgan, 1996). The extent of retardation and exchange depends on the nature of the sediments, the chemicals in solution and chemicals already sorbed on the sediments.

The surface sediments of Long Island are dominantly glacial sand consisting of 95% quartz. The sorption capacity of quartz is low but most sand particles are covered with iron stained coatings, which is typical of coastal plain sediments in northeastern USA (Holmen and Gschwend, 1997; Coston et al, 1995; Wood et al, 1990; Ryan and Gschwend, 1992). These iron-stained coatings have been shown to control the sorption capacity of the sediments (Coston et al, 1995).

Studies of coated sand in environments similar to those of Long Island were conducted in Massachusetts (Coston et al, 1995 and Wood et al, 1990) and in Central New Jersey (Ryan and Gschwend, 1992). The coatings consist of clay minerals (kaolinite, illite), iron hydroxides and organic material. Coston et al (1995) suggested an authigenic origin for coatings in glacial sediments in Cape Cod, that is the minerals formed in place. Ryan and Gschwend (1992) suggested an illuvial origin for coatings on sands in New Jersey, that is the particles were transported to the site and accumulated on the grains.

It is important to know the composition of coatings, because different materials have different cation exchange capacity and surface area. The proportion of the different minerals and organic matter in the coatings determines the cation exchange capacity and the sorption distribution coefficient of the coatings. For example, organic material is the major sorbent for hydrophobic organic compounds (HOC) that also has high cation exchange capacity.

A multi-method approach was used in this study to characterize the coatings. The coated grains were examined with Scanning Electron Microscopy (SEM) to characterize their morphology. X-ray diffraction analysis (XRD) was used to identify the clay mineral assemblage. Transmission Electron Microscopy (TEM) was used to identify the chemical and mineralogical composition of the clays. Total organic carbon concentration (TOC) and surface area (SA) were measured in the coatings and the whole sand.

Hydrophobic organic compounds (HOC) are common contaminants in soils and sediments (Luthy et al, 1997, Holmen and Gschwend, 1997). HOC sorption is a critical process controlling the fate of these chemicals in ground water. It is important to be able to predict the transport properties of HOC for choosing effective remediation procedures. The distribution coefficients (Kd) were measured to estimate capacity of sand to
sorb HOC. Holmen and Gschwend (1997) suggested that most of the organic matter in sand is concentrated in the coatings and this organic matter is the main sorbent for HOC.

Knowing the cation exchange capacity of sediments and the distribution of the exchangeable cations in the unsaturated zone will allow modeling the behavior of cations in the soil for evaluating the effects of, for example, acid rain and nitrate contamination of groundwater. Acid rain affects northeastern USA and North Europe (Likens 1996; 1998; Larsen, 1998; Hyman 1998). As the result of acid rain deposition where $H^+$ and $Al^{3+}$ ions displaced $Ca^{2+}$ and $K^+$, the soil becomes depleted in these cations and enriched with $Al$ and hydrogen. Plants grown on such soils suffer from lack of nutrients, low pH and high amounts of poisonous $Al$.

Nitrate contamination of groundwater is a problem in some heavily populated areas of Long Island where septic tanks or cesspools are used. Effluent from septic tanks or cesspools is enriched with ammonium ion ($NH_4^+$). Ammonium ion has high sorption affinity and can be preferably sorbed onto sediments surrounding a cesspool (Ceazan, 1989). Under oxidizing conditions ammonium ion ($NH_4^+$) is converted to nitrate ion ($NO_3^-$); this nitrate ion then infiltrates the groundwater. Knowing the cation exchange capacity of the sediments that may be surrounding a cesspool will make it possible to evaluate the amount of nitrogen as ammonium may be absorbed around cesspools.

For this study samples were selected from a range of geologic settings and depths within the unsaturated zone. These settings include: sandy soil samples from an outwash plain, medium-coarse sand from a glacial moraine and a glacial outwash fan, and fine sand from glacial lacustrine sediment. A continuous core consisting of silt, sand and gravel was taken from a glacial stream channel to determine how the distribution of exchangeable cations (Ca, Mg, K, Ca, Na, Mn, Fe, and Al) changes with depth in one locality.

Return to Table of Contents

Chapter 1. Methods.

Samples.

Soil and sediment samples were taken from various locations on Long Island to a depth of 12 m below the surface. Sediments vary in grain size from gravel to silt. Soil samples were taken from Fox Pond in Manorville. Sediments were taken from construction sites in South Setauket and Port Jefferson, and from a beach cliff at David Weld Preserve in Nissequogue. In addition, a continuous Geoprobe core was collected at the Cathedral Pines County Park, in Yaphank.

Samples from Port Jefferson construction site (lat. 40°56’3”N., long.73°03’36”W).

Samples 1 and 5 were taken in Port Jefferson east of Sheep Pasture road near the extension of Willis Avenue north of the Harbor Hill moraine.

Sample 1 (100-120cm below the surface) consists of bright brown, coarse sand. The grains are heavily coated.

Sample 5 (160-180cm below the surface) consists of light brown to beige, medium sand to gravel.

Samples from South Setauket construction site, (lat.40°54’54”N., long.73°06’13”W.).

Samples 6 and 7 were taken from South Setauket. The site is located across the street from #6 Poet lane in a
glacial outwash fan.

Sample 6 (140-150cm below the surface) consists of medium-coarse, orange-brown sand with layers of finer, light colored sand.

Sample 7 (200-220cm below the surface) consists of coarse, dark brown sand. Some grains are coated and some are clear.

**Core from Cathedral Pines County Park (lat.40°52′39″N., long.72°56′39″W), Yaphank.**

A continuous core of sediments from 80cm to 6m below the surface was collected by Geoprobe. Near surface samples were taken from a pit in the woods nearby. The geologic environment is a glacial stream channel. The water table was about 6m below the surface.

Sample 11 (0-30cm below the surface) - surface soil horizon. Sample is dark brown, dominantly clay and organic matter, a lot of plant material.

Sample 12 (30-60cm below the surface) - brown silt, rich in organic material

Sample 13 (60-80cm below the surface) - light brown, fine sand-silt contains pieces of partly decomposed plant material.

Sample 14 (90-120cm below the surface) - bright, brown-yellow, medium sand with some gravel and clay.

Sample 15 (150-180cm below the surface) - light brown, homogeneous, well sorted medium sand

Sample 16 (210-240cm below the surface) - light brown very heterogeneous medium sand to gravel.

Sample 17 (270-300cm below the surface) - gray-brown coarse sand contains some coated grains and some clear grains.

Sample 18 (340-360cm below the surface) - gray-beige coarse sand to gravel compacted (hard to remove sample from the tube).

Sample 19 (390-420cm below the surface) - yellow-brown, coarse sand, less gravel compared to 340-360cm sample.

Sample 20 (450-480cm below the surface) - light brown, medium-coarse sand.

**Samples near Fox Pond (lat. 40°53′28″N., long.72°48′46″W.), Manorville.**

Soil samples were taken from near Fox Pond on the glacial outwash plain. The samples were collected from a pit. Soil is very sandy.

A1 (5-20cm)- Below the organic O horizon, contains a lot of partly decomposed organic material (leaves, needles, roots), gray-brown, sandy.

A2 (20-30cm)- depleted, eluvial horizon, gray-light gray, very sandy, containing significantly less amount of organic matter than sample A1.
B (30-50cm)- illuvial horizon, bright brown-orange color, heavily coated sand.

**Samples from beach cliff at David Weld Preserve (lat.40°57’58"N., long.73°9’4"W), Nissequogue.**

Samples were taken from a beach cliff face (lat.40°57’58"N., long.73°9’4"W.). These samples are from a glacial lacustrian environment.

8-10m below the surface – yellow-red colored fine, well sorted sand characterized with climbing ripples.

10-12m below the surface - pale, fine sand without distinctive coatings on the grains surfaces.

**Analytical methods**

**Cation Exchange Capacity**

0.1 M BaCl₂ solution was used to displace exchangeable cations from sediment samples following the procedure of (Hendershot, 1986). Solutions were prepared from 99.999% pure BaCl₂ powder from Alfa Aesar. This table shows concentration of elements in the BaCl₂ powder.

<table>
<thead>
<tr>
<th>elements</th>
<th>Concentration (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Mg</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Mn</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Al</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Fe</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Na</td>
<td>&lt;1</td>
</tr>
<tr>
<td>K</td>
<td>&lt;100</td>
</tr>
</tbody>
</table>

Pure BaCl₂ was used to reduce concentration of the elements in blank solution. Ba²⁺ ion was chosen instead of NH₄⁺ because of its higher exchange affinity. Samples were prepared following the procedure outlined in Hendershot (1986). Three to four grams of sediment were placed in 45 ml centrifuge tube with 40 ml of BaCl₂ solution so that the ratio of sediment: solution was approximately 1: 10. The samples in the BaCl₂ solution were put in ultrasonic bath for 60 min then filtered. The supernatant was collected and exchangeable Ca, Mg, Na, K, Al, Fe, Mn were measured by a Beckman Instruments Direct Current Argon Plasma Emission Spectrometry (DCP-AES). The DCP analyses were done following a procedure described by McDaniel (1992). Different elements have different optimum conditions under which they may be analyzed. The major elements (Mg, Mn, K, Na, Al, Fe) were run together on a multi-element cassette. The signal was peaked on Mg. Ca was run separately with peaking on Ca. The four standards and the blank were prepared with the
same 0.1 M BaCl₂ solution as used for the sample preparation. All standards were prepared from a master solution by diluting certain amount of master solution with 0.1M BaCl₂. The concentration of the highest standard was at least 10 times higher than the concentration of the highest sample.

Concentration of the elements in the master solution.

<table>
<thead>
<tr>
<th>element</th>
<th>(ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>397</td>
</tr>
<tr>
<td>Mg</td>
<td>93.7</td>
</tr>
<tr>
<td>Fe</td>
<td>43.3</td>
</tr>
<tr>
<td>Mn</td>
<td>26.5</td>
</tr>
<tr>
<td>Na</td>
<td>161.6</td>
</tr>
<tr>
<td>Al</td>
<td>93.5</td>
</tr>
<tr>
<td>K</td>
<td>49.2</td>
</tr>
</tbody>
</table>

Spex Plasma Standards were used for preparation of the master solution. The calculated amount of 0.2 BaCl₂ was added in the master solution so that the concentration of the Ba²⁺ ion in the master solution was identical to the concentration of Ba²⁺ ion in the solution used for sample preparation (0.1 M BaCl₂). Each sample solution was analyzed 2 times. The analytical uncertainty for most samples is less than 5%, for concentrations well above detection limit. For K and Ca analytical uncertainty is approximately 10%.

Separation of the coatings

Coatings on the samples 1, 5, 6, 7 and B were separated from sand using an ultrasonic probe. Sediments were placed in 100ml plastic beaker with 40-50ml of distilled water and sonicated for 15-20 min. The supernatant with coatings was transferred into 45ml centrifuge tube. Another 40-50ml of water was added to the beaker with sediments and sonicated for 15-20 min and supernatant was collected again. This procedure was repeated up to 4 times that grains were clear (lost color). The supernatant was centrifuged for 1hr at 2000rpm. Most of the coatings settled on the bottom of the centrifuge tube. Supernatant was removed by pipette. Coatings were dried in the oven at 50°C.

pH measurement

Water and BaCl₂ pH was measured in the core from the Cathedral Pine County Park and samples from the South Setauket and Port Jefferson, following the procedure described in Jackson (1974). Three to four grams of sediment were placed in 45ml centrifuge tube with 40 ml of 0.1M BaCl₂ solution or distilled water. The ratio of sediment: solution was approximately 1: 10. BaCl₂ or distilled water suspension was put in ultrasonic
bath for 60 min then filtered. The supernatant was collected and pH was measured using Titra-Line alpha titration unit.

**X-ray powder diffraction (XRD)**

The fine coated sand from beach cliff at David Weld Preserve (sample 10) was chosen for clay identification. The < 2m m clay fraction was separated from both the whole sand and the coatings. Clay minerals were separated from carbonates and iron oxides. Carbonates were removed by heating samples (< 2m m) in a sodium acetate-acetic acid buffer at pH 5 (Jackson, 1974). The buffered solution was prepared by dissolving 82g of sodium acetate in about 900ml of distilled water adding 27ml of glacial acid and adjusting pH to 5 by adding sodium hydroxide or acetic acid and then diluting with distilled water to 1L. Ten grams of sample were added to a beaker with 250 ml of buffered solution. The solution was stirred on a hot plate at low enough temperature to avoid boiling. The evidence of complete reaction is absence of bubbles. Sample was then washed several times with distilled water by centrifuging. We did not observe any evidence of carbonate in these samples.

It was necessary to remove iron oxides, because we used CuKa radiation. Fluorescent X-rays from Fe produce a high background that masks peaks. Also iron oxides cement the clay particles together inhibiting dispersion. Iron oxide was removed chemically with citrate-bicarbonate-dithionite (Jackson, 1974). The carbonate free samples were placed in a beaker in which 40-ml of 0.3N Na-citrate solution and 5 ml of 0.1 N NaHCO₃ were added. The suspension was warmed to 80°C on a hotplate, one gram of solid Na₂S₂O₄ was then added into the solution. The suspension was stirred constantly for the first minute and occasionally for 15 min. then 10-ml of a saturated NaCl was added. The suspension was centrifuged with distilled water at least 5 times. The resulting material was then ultrasonically disaggregated.

The fraction < 2m m was separated for XRD by centrifuging sample in 45 ml tube at 750 rpm for 3.3 min. The supernatant liquid was then decanted into another centrifuge tube. The centrifuge tube containing the clays fraction < 2m m was then centrifuged at 2000rpm for 20 min. The supernatant was removed. The residue containing the clay minerals was then pipetted onto a glass slide and left to dry at room temperature.

X-ray patterns were recorded from 3 to 50 2q degrees using CuKa radiation using a Scintag powder diffractometer operated at 45kV and 25mA.

**Transmission Electron Microscopy (TEM)**

Transmission electron microscopy analysis was made on the separated coating from one heavily coated sand (sample1) from Port Jefferson. This sample was sonicated in deionized water for 20 min. One drop of the dispersed coatings was then pipetted onto a porous carbon film grid and left covered to dry at room temperature. The TEM analysis follows that outlined by Barber, Reeder, and Smith (1984). The JEOL 200-CX TEM instrument fitted, with an EDS systems for micro-chemical analysis, was operated at an accelerating voltage of 200 keV. The sample was placed in a low-background graphite sample holder tilted at 35 degrees. Counting times were 200 sec. Integrated intensities of peaks were determined after background subtraction. Integrated peak intensity ratios were converted to atomic concentration ratio using the Cliff and Lorimer relation (1975). The Cliff and Lorimer give the equation:

\[ \frac{C_A}{C_B} = k_{AB} \cdot \frac{I_A}{I_B} \]  

(eq. 1)

Where \( C_A \) and \( C_B \) are the atomic concentrations of elements and A and B in a given compound, \( I_A \) and \( I_B \) are the intensities of emission lines of those elements and \( k_{AB} \) is a proportionality factor. The \( k_{AB} \) is
experimentally determined for a standard compound of known composition. Si is element B, because of its ubiquitous occurrence in these samples.

**Scanning Electron Microscopy (SEM)**

Untreated coated sand (samples 1 and 5 from Port Jefferson and sample 10 from the beach cliff at David Weld Preserve) were characterized using JEOL scanning microscope 5300 in the University Microscopy center at SUNY Stony Brook. The dry loose sand sample was placed on a holder covered with a carbon film and coated with gold prior to SEM analysis.

**Sorption of hydrophobic organic compounds**

The sorption partition coefficient between solids and water for hydrophobic organic compounds was determined on whole sand, separated coatings, grains with coatings removed, whole sand treated with ultrasonic probe but with removing the coatings and sand with iron compounds removed were studied. Hot HCl extraction was used to remove iron compounds. Extraction was done following the procedure described in Costen et al, (1995). The samples were leached with 4M HCl (3ml of acid per gram of sediment) for one hour at 100°C in Teflon beakers. Then the sediments were placed in centrifuge tubes and washed by centrifuging with distilled water at least 6 times. Then the sediments were air-dried.

The method used for determining sorption of hydrophobic organic compounds onto the sediments following the principals of a common headspace partitioning designed for determining partition coefficients of organic compounds and hydrophobic interactions in proteins (Wishnia and Pinder, 1966).

Hexachlorobenzene (HCB) was chosen as the hydrophobic organic compound, because HCB is highly sorbed on solids and is not degraded by microorganisms. $^{14}$C - labeled HCB (15.9 mCi/mmol) was used as sorbate.

A vessel was designed for the experiment. An inner space containing pure water is isolated from an outer space containing the sediment suspension. The two compartments share the common headspace through which volatile organic compounds can partition. At the equilibrium, dissolved phases of HCB are equal in an inner and an outer compartments. The amount of sorbed HCB can be determined by comparing the concentration of dissolved compounds and the total concentration (dissolved and partitioning) of the outside solution in the vessel with sediments; or by the difference in concentrations of the inner compartment (dissolved only) in the vessel with sediments and control vessel (see calculations below). The top of the vessel was sealed with an aluminum foil under a screw-capped lid. Controlled mass-balance studies showed no significant leakage of HCB out of the vessels over the first 48 hours. However, slow leakage was apparent for longer periods. Therefore, sorption was limited to 48 hours. The vessels were treated with a solution of $K_2Cr_2O_7$ in concentrated $H_2SO_4$ to oxidize and remove any organic material in the bottles between uses. The vessels were then washed with distilled water, acetone, hexane and dichloromethane (DCM). The vessels were air-dried for 2 hours and a known mass of sediment was then placed in an outer part of the bottle. Ten ml of distilled water was added into both an inner and an outer parts. The vessels were placed into an ultrasonic bath for 10 min. Then 7.5 microliters of $^{14}$C labeled HCB (159 mCi/ml) in methanol were added into an outer part of the vessel. The vessels were closed tightly and put on the shaker at the constant temperature (25°C). Duplicates for the control vessels and the vessels with samples were prepared each time.

Kinetic sorption experiments were conducted. Pure water in both inside and outside compartments and the sediments samples were equilibrated for 2 hours, 8 hours, 24 hours, 72 hours, 10 days and 30 days. We found out that system needed just over 24 hours for the dissolved phase to reach equilibrium. When the
system is at equilibrium the concentration of $^{14}$C labeled HCB is identical in the inner and in the outer part of the vessel (checked using the control vessels). There was a slight loss of HCB after 72 hours. This loss increased with time. Therefore, we used 48 hours equilibration in all of our studies.

The control vessel for each experiment consistently showed equilibration and good mass-balance at 48 hours. After 48 hours the replicated 2ml aliquots were taken from the inner part of the vessel with sediments and from both the inner and an outer part of the control vessel. Samples were placed into scintillation vials and 10 ml of ULTIMA GOLD LLT cocktail was added. C$^{14}$ was counted on a LKB 1217 RACKBETA Liquid Scintillation counter.

The distribution coefficient ($K_d$) was calculated based on assumption that

$$M_{\text{total}} = M_{\text{water}} + M_{\text{sorbed}} + M_{\text{vapor}} \quad \text{(eq. 2)}$$

Where $M_{\text{total}}$ is the total mass of HCB added into the system, $M_{\text{water}}$ is the mass of HCB dissolved in the water, $M_{\text{sorbed}}$ is the mass of HCB sorbed onto the sediments and $M_{\text{vapor}}$ is the mass of HCB in the vapor phase of the vessel. Experiments were done with $^{14}$C labeled HCB and the measured disintegrations per minute (DPM) were proportional to mass.

$$DPM_{\text{total}} = DPM_{\text{water}} + DPM_{\text{sorbed}} + DPM_{\text{vapor}} + DPM_{\text{wall}} \quad \text{(eq. 3)}$$

$DPM_{\text{total}}$ was measured. $DPM_{\text{water}}$ was measured in the vessel containing the sediments. $DPM_{\text{wall}}$ was found to be negligible.

For soluble compounds like HCB the vapor phase concentration is directly proportional to the dissolved phase through Henry’s Law (Schwarzenbach et. al, 1993). $DPM_{\text{vapor}}$ in the treatment can be calculated by determining the ratio of HCB in the vapor to that in the water in the control vessels

$$\frac{(DPM_{\text{total}} - DPM_{\text{water}})}{DPM_{\text{water}}} \times DPM_{\text{water sample}} \quad \text{(eq. 4)}$$

$DPM_{\text{vapor}}$ on the sediments was calculated as

$$DPM_{\text{sorbed}} = DPM_{\text{total}} - (DPM_{\text{water sample}} + DPM_{\text{vapor}}) \quad \text{(eq. 5)}$$

The fraction of the sorbed HCB ($f_{\text{sorbed}}$) was calculated.

$$f_{\text{sorbed}} = \frac{DPM_{\text{sorbed onto sediments}}}{DPM_{\text{sorbed onto sediment}} + \frac{1}{2} DPM_{\text{water sample}}} \quad \text{eq. 6}$$

Half the $DPM_{\text{water sample}}$ was used in the calculations because the sediments were placed only into the outer part of the bottles, which contains half the total volume of water. The fraction HCB dissolved in the water was calculated as one minus fraction HCB sorbed onto the sediments.
\[ f_{\text{dissolved}} = 1 - f_{\text{sorbed}} \]  

(eq. 7)

The distribution coefficient \( (K_d) \) was calculated as

\[ K_d = \frac{f_s}{f_d} \times \text{(mass (of sediments) / volume (of water))} \]  

(eq. 8)

Where \( f_s \) is the sorbed fraction of HCB, \( f_d \) is the fraction of HCB dissolved in the water. The mass of the sediments used for experiments was expressed in grams and the volume of distilled water, added into the outer part of the bottle, expressed in ml (in our case it was 10ml).

**Surface area measurements**

The surface area was analyzed for sand samples 1, 5, 6 and 7 and for coatings separated from the same samples. Samples were measured using a multi-point BET (Brunauer-Emmett-Teller) method. Samples were analyzed at the Pennsylvania State University Material Characterization Laboratory by Tom Rusnak.

**Total Organic Carbon (TOC)**

Total organic carbon (TOC) was analyzed in whole sand and coatings for samples 1, 5, 6 and 7. David Hirschberg did the analyses at the Marine Science Research Center SUNY Stony Brook. Total organic carbon was measured on a CHN Elemental Analyzer. The whole sand samples were ground to a fine powder followed by 2M HCl treatment to remove carbonate. The samples were then washed with distilled water at least 6 times and dried at 50\(^\circ\)C.

One portion of the coatings was untreated. Another portion was treated using the procedure of Mayer (1994). In this procedure the coatings were placed in a beaker and kept in a dessicator with concentrated HCl overnight. The coatings were then dried overnight at room temperature and then dried in an oven at 70\(^\circ\)C. This method avoids leaching organic carbon bonded to iron compounds.

**Chapter 2 Cation exchange capacity**

**Results**

One objective of this study is to evaluate the cation exchange capacity (CEC) and the relative proportion of major exchangeable cations in Long Island glacial sediments. "The ion exchange capacity of a soil (or sediment) is the number of moles of sorbed ion charge that can be desorbed from unit mass, under given conditions of temperature, pressure, soil solution composition (including pH), and soil solution mass-ratio" (Sposito, 1994). Cation exchange capacity is a function of grain size, amount of organic matter, amount of coatings on the grains and mineralogy of the sorbing material. Different materials have different CEC (Table 1). Organic matter has the highest CEC (200-400 meq/100g). Iron compounds (goethite and hematite) also have high CEC up to 100 meq/100g. The CEC of clay minerals varies in a wide range: from kaolinite (CEC 3-15 meq/100g) to smectite (80-150 meq/100g).

[Link to tables for chapter 2 data.](#) This is a large file about 200 Kb.

The CEC of Long Island sediments in this study varies from 0.85 meq/100g to 21.4 meq/100g. Most of the grains consist of quartz. The quartz grains often have a coated surface consisting of clay, organic matter and
iron oxides and hydroxides. The weight fraction of coating material relative to the whole sample varies from 0.8-13%.

Measured cation exchange capacity (CEC) values are shown in Table 3 and Figures 1 and 2. Grain size is an important factor in determining CEC. Sample 10, which is fine sand, has the highest CEC (21.3 meq/100g). While sample 16, which is coarse sand to gravel, has the lowest CEC (0.85 meq/100g). This most likely is because fine sand has a larger surface area than does coarse material and also because fine sand includes a more significant fraction of clay minerals, which have quite high CEC (Table 1).

---

**Fig. 1** Cation exchange capacity (CEC) of the core from Cathedral Pine County Park

**Fig. 2** Cation exchange capacity of the sediments from Port Jefferson (sample 1), South Setauket (samples 6 and 7), soil near Fox Pond and the beach cliff at David Weld Preserve
For sample B, a sandy soil, CEC was measured on the total sample, on the coatings and on the naked grains (Table 2). Naked grains are grains that have had the coating removed by sonification. The coatings make up 13 weight percent of this sample. The CEC of the whole sample is 11.7 meq/100g. The CEC of the coatings is 78.3 meq/100g. The CEC of the naked grains is 0.29 meq/100g. A mass-balance calculation shows that the coatings contribute 87% of the CEC. We may conclude that coatings affect the exchange capacity significantly.

For both the core from Cathedral Pine County Park and the soil profile near Fox Pond CEC decreases along with organic matter concentration with depth.

The CEC for the samples from the core have the highest values at a depth of 0-30 cm (18.3 meq/100g). This upper part of the soil horizon is enriched in organic material and clay. With increasing depth in the core CEC continually decreases. The sample from a depth of 150-180 cm (sample 15) has a CEC of 1.32 meq/100g. This variation reflects both a change in grain size (from silt to coarse sand-gravel) and a decreasing fraction of organic matter with depth.

The soil near Fox Pond is sandy. The highest CEC was observed in the organic enriched A1 horizon (14.7 meq/100g). The lowest CEC was observed in the eluvial A2 horizon (9.20 meq/100g). An intermediate CEC value was observed in the illuvial B horizon (horizon of oxides accumulation) (11.7 meq/100g). The illuvial B horizon is enriched with Fe and Al oxides and clay material. The A2 horizon may be depleted in cations because soil solutions with low pH were derived from acid rain or the decomposition of organic matter resulting in the formation of humic, fulvic and other organic acids. The acid-leached cations may then have accumulated in the illuvial B horizon.

The soil from the Cathedral Pines County Park is silty and is more enriched with organic matter compared to the Fox Pond soil. The CEC of the A1 organic horizon is 18.3 meq/100g. The eluvial depleted horizon is not as obvious in Cathedral Pine soil as it is in the Fox Pond soil.

The proportion of exchangeable cations as a function of depth is shown for the core from Cathedral Pines County Park in Table 4 and in Figure 1. The upper (0-30 cm) organic soil horizon (sample 11) has the highest fraction of exchangeable Ca (8% of total CEC). At a depth of 90-120 cm (sample 14), the Ca dropped to less than detection (<0.002 meq/100g).

The relative proportion of organic matter decreases with depth. Likens (1998) has shown that in New Hampshire the exchangeable Ca concentration in soils is directly related to the organic matter content of soil.

The concentration of exchangeable Al changes significantly with depth (Table 4, Figure 1). The Al in the sediments from 0-120 cm makes up to 75 to 82% of the total CEC (Table 4). At depths greater than 150 cm the exchangeable Al rapidly decreases to less than detection (<0.0015 meq/100g).

High proportions of exchangeable Al were also observed in the upper 2 meters of the soil sediments from South Setauket and Port Jefferson (Table 4, Figure 2).

The percentage of exchangeable Na increases with depth from 7-10% at the top to 55-78% at the bottom of the sequence (Table 4, Figure 1).

The exchangeable Fe ion concentration is low (in most cases less than detection) along the profile (Table 4, Figure 1). This may be because most of the iron exists in immobile (Fe$^{3+}$) form.
Actual and potential acidity were measured on the core from the Cathedral Pines County Park and for samples from Port Jefferson and South Setauket (Table 5).

Actual acidity is a measure of the hydronium ion concentration (pH) in a soil solution or in a soil-water suspension. Al and Fe occurring as amphoteric hydroxides react with water to release $\text{H}_3\text{O}^+$ (Stumm and Morgan, 1996).

$$\text{Al}(\text{H}_2\text{O})_6^{3+} + \text{H}_2\text{O} = \text{Al}(\text{H}_2\text{O})_5\text{OH}^{2+} + \text{H}_3\text{O}^+ \text{ (eq. 1)}$$

Potential acidity is a measure of a sediments ability to produce exchangeable hydronium ($\text{H}_3\text{O}^+$) ion by cation exchange with salt solutions, in this case 0.1M BaCl$_2$, (Kovda and Rosanov, 1988).

Hydronium ion concentration in the soil for actual acidity was calculated based on the pH of the aqueous solution resulting from the mixing of deionized water with soil.

The hydronium ion concentration for the potential acidity was calculated based on the pH of a mixture of 0.1 molar BaCl$_2$ and soil (Table 6). In the upper part of the sequence (0-120 cm) the concentration of $\text{H}^+$ in the BaCl$_2$ extraction (potential acidity) is higher than that in the $\text{H}_2\text{O}$ extraction (actual acidity). At greater depths (120-480 cm) the concentration of hydronium ion based on actual acidity (water extraction) is greater than that based on potential acidity (BaCl$_2$ extraction) (Table 6).

In the upper 120cm of the profile Al ions make up to 82% of the exchangeable cations and the concentration of hydronium ions based on potential acidity is always higher than that for actual acidity. When the fraction of exchangeable Al drops to less than detection at 180cm the concentration of hydronium ion related to water extraction (actual acidity) exceeds that related to the salt extraction (potential acidity).

Therefore, correlation of hydronium concentration in the salt extraction (potential acidity) with distribution of exchangeable Al was observed. What causes the excess of hydronium ion in salt (BaCl$_2$) extraction compared with water extraction in the upper 150 cm of the core? First of all, distilled water does not have cations, which will displace exchangeable cations including hydronium ion.

Ba$^{2+}$ ion has a high sorption affinity (Stumm and Morgan, 1996). Possibly, the BaCl$_2$ extraction removes mainly the exchangeable hydronium ion but another part originated from Al hydroxide dissociation. The exchangeable Al may form hydrated cations $\text{Al}(\text{H}_2\text{O})_6^{3+}$. As a result of the interaction with water these hydrated cations produce hydronium ions in the solutions (Stumm and Morgan, 1996; Kovda and Rosanov, 1988), (see equation 1).

Generally, the concentration of hydronium ion is higher in the upper part of the core compared to the lower part for both actual and potential acidity. The upper part of profile is enriched with organic matter. Organic acids and humic and fulvic acids may be responsible for higher $\text{H}^+$ concentration in the top part of the core compared to the bottom (Kovda, Rosanov, 1988).

Discussion

In the core from the Cathedral Pine County Park Ca made up 8% of exchangeable ions in the upper 30 cm, at greater depth the proportion of Ca decreased significantly. Which factors control the Ca ion distribution along
the profile?

Ca is a plant nutrient and its occurrence is directly related to the distribution of organic matter and root penetration (20% of Ca input is by root discharge) (Likens, 1998). Most Ca ion in Long Island sediments comes from dry precipitation (Xin, 1993, Lawrence 1998). Weathering of parent material is not a significant source for Ca in Long Island soils. Long Island sediments are typically sandy, consist mostly of quartz and contain insufficient amount of primary minerals, which can release Ca ion during weathering processes.

Also the soil depletion of Ca could be the result of leaching due to input of acid rain (Likens et al, 1998). The chemistry of bulk precipitation and stream water has been measured continuously at Hubbard Brook Experimental Forest (HBEF) (Likens, 1996). Likens, (1996, 1998) and Finzi, (1998) have shown that the large decline of Ca in both precipitation streamwater, and the depletion in the Ca in the soil since 1963. According to Likens the net biomass storage of Ca in the HBEF decreased from 202 to 54 mol/ha-yr in 1964-69 and 1987-92 respectively. Probably, the low fraction of Ca in soil complex of Long Island sediments reflects both the decline of Ca in dry precipitation (the main source of base cations on Long Island) and leaching Ca away from the soil profile due to effect of acid rain (Likens, 1996,1998).

Why is Al ion the main exchangeable cation (up to 82% of total CEC) within 120 cm of the surface? What is the explanation for such high proportion of Al in an upper part of the sequence? According to Matzner (1998) even in the soil with low carbon content Al bounded with organic matter is the major source of Al in soil solution. This may explain high concentration of Al in the upper part of the sequence. The upper part is enriched with organic matter, with depth concentration of organic matter decreases the exchangeable Al concentration does the same. Another possibility is that Al enrichment combined with Ca depletion is an effect of acid rain. Acid rain has an average pH of 4.05-4.3 in Long Island (Likens, 1996). When rainwater with such low pH drains into the soil it dissolves minerals, such as, gibbsite, which allows free Al ions appear in the soil solution (Stumm and Morgan, 1996). The base cations in soil exchangeable complex are replaced by the positively charged hydrogen and Al ions from the soil solution. As long as the soil has an abundant supply of base cations this buffering system, known as Cation Exchange Capacity, protects the soil from acid rain. The natural reserve of cations becomes depleted if soil is exposed to acid rain for too long time. As result soil becomes enriched with Al and H ions. Another possibility is, that organic acids formed during leaf and needle decomposition, may create acidic conditions in the soil profile. This leads to the mineral dissolution and the release of mobile Al. Possibly, both processes explain high fraction of Al ion in exchangeable complex of Long Island sediments but we do not have enough information to distinguish between them. Other studies also show high Al fraction in soil exchangeable complex in different region of northeastern USA (Larsen, 1998; Likens 1996, 1998).

Some of Long Island sediments have high CEC (up to 21.3 meq/100g). Results, reported by Lani (1996), show even higher CEC for some Long Island sediments. The fine-coarse sand from upper glacial has CEC up to 60 meq/100g and fine-medium sand from Magothy formation has CEC 70 meq/100g. But sediments are sandy and mostly composed of quartz. What is the major source of exchangeable cations? This study indicates that coatings on the sand surface mainly responsible for the cation exchange. Coatings made up to 13 % of sediments. The coatings consist of illite, kaolinite and chlorite with minor amount of organic material (TOC is up to 0.7 %) and iron compounds. Combination of these three components hardly can show such high CEC. Illite, kaolinite and chlorite do not have high CEC and only organic matter and iron compounds have high CEC (Table 1), but their fraction in the coatings is not large enough to give such high CEC for sand. To answer on this question the wider variety of the sediments need to be examined.

We identified that CEC of Long Island sediments varies from 0.85 to 21.3 meq/100g. Coatings are a major
water and BaCl₂ extractions are higher in the upper part of sequence. Concentration of hydrogen ion in BaC-I₂ extraction correlates with exchangeable Al concentration along the core.

Return to Table of Contents

**Tables for Chapter 2 Cation Exchange Capacity**

**Table 1.** Cation Exchange Capacity of the different types of material
(modified from Appelo and Postma, 1993 and Velde, 1995).

<table>
<thead>
<tr>
<th>Type of material</th>
<th>CEC (meq/100g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaolinite</td>
<td>3-15</td>
</tr>
<tr>
<td>Chlorite</td>
<td>10-40</td>
</tr>
<tr>
<td>Illite</td>
<td>10-40</td>
</tr>
<tr>
<td>Smectite</td>
<td>80-150</td>
</tr>
<tr>
<td>Organic matter</td>
<td>150-400</td>
</tr>
<tr>
<td>Goethite &amp; Hematite</td>
<td>up to 100</td>
</tr>
</tbody>
</table>

**Table 2.** Results of the measurement of
cation exchange capacity for sample B

<table>
<thead>
<tr>
<th>Material</th>
<th>CEC meq/100g.</th>
<th>Weight Fraction</th>
<th>Relative Proportion of CEC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coatings</td>
<td>78.3</td>
<td>13%</td>
<td>97%</td>
</tr>
<tr>
<td>Naked Grains</td>
<td>0.29</td>
<td>87%</td>
<td>3%</td>
</tr>
<tr>
<td>Calculated Whole Sample</td>
<td>10.4</td>
<td>100%</td>
<td>100%</td>
</tr>
<tr>
<td>Measured Whole Sample</td>
<td>11.7</td>
<td>100%</td>
<td>100%</td>
</tr>
</tbody>
</table>
**Table 3.** Cation Exchange Capacity (CEC) of the sediments from Port Jefferson, South Setauket, David Weld Preserve, Fox Pond and the core from Cathedral Pine County Park.

<table>
<thead>
<tr>
<th>Depth (cm)</th>
<th>Samples</th>
<th>Ca</th>
<th>Mg</th>
<th>Fe</th>
<th>Mn</th>
<th>Na</th>
<th>Al</th>
<th>K</th>
<th>Total CEC</th>
</tr>
</thead>
<tbody>
<tr>
<td>100-120</td>
<td>1</td>
<td>0.91</td>
<td>0.32</td>
<td>0.82</td>
<td>0.09</td>
<td>1.34</td>
<td>2.62</td>
<td>0.31</td>
<td>6.40</td>
</tr>
<tr>
<td>160-180</td>
<td>5</td>
<td>1.00</td>
<td>0.42</td>
<td>0.80</td>
<td>0.04</td>
<td>1.42</td>
<td>2.29</td>
<td>0.38</td>
<td>6.35</td>
</tr>
<tr>
<td>120-140</td>
<td>6</td>
<td>0.78</td>
<td>0.18</td>
<td>0.49</td>
<td>0.03</td>
<td>1.55</td>
<td>0.81</td>
<td>0.19</td>
<td>4.03</td>
</tr>
<tr>
<td>200-210</td>
<td>7</td>
<td>1.53</td>
<td>0.16</td>
<td>0.09</td>
<td>0.07</td>
<td>2.75</td>
<td>0.22</td>
<td>0.15</td>
<td>4.98</td>
</tr>
<tr>
<td>800-1000</td>
<td>9</td>
<td>8.68</td>
<td>7.38</td>
<td>0.13</td>
<td>0.01</td>
<td>0.64</td>
<td>0.16</td>
<td>0.26</td>
<td>17.3</td>
</tr>
<tr>
<td>1000-1200</td>
<td>10</td>
<td>10.51</td>
<td>8.78</td>
<td>0.14</td>
<td>0.02</td>
<td>1.23</td>
<td>0.19</td>
<td>0.42</td>
<td>21.3</td>
</tr>
<tr>
<td>5-20</td>
<td>A1</td>
<td>3.74</td>
<td>0.15</td>
<td>0.69</td>
<td>0.14</td>
<td>0.62</td>
<td>8.75</td>
<td>0.57</td>
<td>14.7</td>
</tr>
<tr>
<td>20-30</td>
<td>A2</td>
<td>1.80</td>
<td>0.06</td>
<td>0.78</td>
<td>0.07</td>
<td>0.30</td>
<td>5.76</td>
<td>0.42</td>
<td>9.20</td>
</tr>
<tr>
<td>30-50</td>
<td>B</td>
<td>1.17</td>
<td>0.05</td>
<td>0.54</td>
<td>0.06</td>
<td>0.19</td>
<td>9.34</td>
<td>0.34</td>
<td>11.7</td>
</tr>
<tr>
<td>0-30</td>
<td>11</td>
<td>1.49</td>
<td>0.60</td>
<td>0.04</td>
<td>0.11</td>
<td>1.82</td>
<td>13.8</td>
<td>0.44</td>
<td>18.3</td>
</tr>
<tr>
<td>30-60</td>
<td>12</td>
<td>0.40</td>
<td>0.30</td>
<td>&lt;DL</td>
<td>0.04</td>
<td>1.36</td>
<td>11.4</td>
<td>0.39</td>
<td>13.9</td>
</tr>
<tr>
<td>60-90</td>
<td>13</td>
<td>0.84</td>
<td>0.50</td>
<td>&lt;DL</td>
<td>0.16</td>
<td>0.93</td>
<td>10.7</td>
<td>0.33</td>
<td>13.4</td>
</tr>
<tr>
<td>90-120</td>
<td>14</td>
<td>&lt;DL</td>
<td>0.22</td>
<td>&lt;DL</td>
<td>0.08</td>
<td>0.65</td>
<td>4.18</td>
<td>0.36</td>
<td>5.48</td>
</tr>
<tr>
<td>150-180</td>
<td>15</td>
<td>&lt;DL</td>
<td>0.13</td>
<td>0.06</td>
<td>0.06</td>
<td>0.88</td>
<td>0.02</td>
<td>0.16</td>
<td>1.32</td>
</tr>
<tr>
<td>210-240</td>
<td>16</td>
<td>&lt;DL</td>
<td>0.11</td>
<td>&lt;DL</td>
<td>0.08</td>
<td>0.52</td>
<td>&lt;DL</td>
<td>0.13</td>
<td>0.85</td>
</tr>
</tbody>
</table>

Exchangeable cations (meq/100g)

<table>
<thead>
<tr>
<th>Depth (cm)</th>
<th>Samples</th>
<th>Ca</th>
<th>Mg</th>
<th>Fe</th>
<th>Mn</th>
<th>Na</th>
<th>Al</th>
<th>K</th>
<th>Total CEC</th>
</tr>
</thead>
<tbody>
<tr>
<td>270-300</td>
<td>17</td>
<td>&lt;DL</td>
<td>0.23</td>
<td>0.12</td>
<td>0.31</td>
<td>0.71</td>
<td>&lt;DL</td>
<td>0.25</td>
<td>1.62</td>
</tr>
<tr>
<td>360-390</td>
<td>18</td>
<td>&lt;DL</td>
<td>0.75</td>
<td>&lt;DL</td>
<td>0.48</td>
<td>1.55</td>
<td>&lt;DL</td>
<td>0.69</td>
<td>3.47</td>
</tr>
<tr>
<td>420-440</td>
<td>19</td>
<td>&lt;DL</td>
<td>0.06</td>
<td>&lt;DL</td>
<td>0.05</td>
<td>0.79</td>
<td>&lt;DL</td>
<td>0.11</td>
<td>1.02</td>
</tr>
<tr>
<td>450-480</td>
<td>20</td>
<td>0.22</td>
<td>0.13</td>
<td>&lt;DL</td>
<td>0.1</td>
<td>0.73</td>
<td>&lt;DL</td>
<td>0.16</td>
<td>1.34</td>
</tr>
</tbody>
</table>
**Table 4.** Relative ion concentration to the total Cation Exchange Capacity. Core from Cathedral Pines County Park.

<table>
<thead>
<tr>
<th>Depth (cm)</th>
<th>Samples</th>
<th>Ca % From total CEC</th>
<th>Mg % From total CEC</th>
<th>Fe % From total CEC</th>
<th>Mn % From total CEC</th>
<th>Na % From total CEC</th>
<th>Al % From total CEC</th>
<th>K % From total CEC</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-30</td>
<td>11</td>
<td>8%</td>
<td>3%</td>
<td>0%</td>
<td>1%</td>
<td>10%</td>
<td>75%</td>
<td>2%</td>
</tr>
<tr>
<td>30-60</td>
<td>12</td>
<td>3%</td>
<td>2%</td>
<td>0%</td>
<td>0%</td>
<td>10%</td>
<td>82%</td>
<td>3%</td>
</tr>
<tr>
<td>60-90</td>
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<td>6%</td>
<td>4%</td>
<td>0%</td>
<td>1%</td>
<td>7%</td>
<td>79%</td>
<td>2%</td>
</tr>
<tr>
<td>90-120</td>
<td>14</td>
<td>0%</td>
<td>4%</td>
<td>0%</td>
<td>1%</td>
<td>12%</td>
<td>76%</td>
<td>7%</td>
</tr>
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<td>150-180</td>
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<td>16%</td>
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<td>0%</td>
<td>14%</td>
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<td>19%</td>
<td>44%</td>
<td>0%</td>
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<td>360-390</td>
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<td>5%</td>
<td>78%</td>
<td>0%</td>
<td>11%</td>
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<tr>
<td>450-480</td>
<td>20</td>
<td>16%</td>
<td>9%</td>
<td>0%</td>
<td>7%</td>
<td>55%</td>
<td>0%</td>
<td>12%</td>
</tr>
</tbody>
</table>

**Table 5.** $\text{BaCl}_2$ and H$_2$O pH values. Samples from Port Jefferson, South Setauket and the core from Cathedral Pines County Park.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Depth(cm)</th>
<th>pH (BaCl$_2$)</th>
<th>pH (H$_2$O)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pine Cathedral County Park</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>0-30</td>
<td>4.28</td>
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<td>60-90</td>
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<td>5.13</td>
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<td>90-120</td>
<td>4.48</td>
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<td>150-180</td>
<td>5.61</td>
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<td>16</td>
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<td>19</td>
<td>420-440</td>
<td>5.84</td>
<td>5.22</td>
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<td>450-480</td>
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<td>Port Jefferson</td>
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<td></td>
<td>South Setauket</td>
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<td>6</td>
<td>120-140</td>
<td>5.52</td>
<td>6.65</td>
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<td>7</td>
<td>200-220</td>
<td>5.84</td>
<td>6.59</td>
</tr>
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</table>
### Table 6. Concentration of hydrogen (H\(^+\)) ion in the core from the Cathedral Pine County Park (H\(_2\)O and 0.1M BaCl\(_2\) extractions).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Depth(cm)</th>
<th>H(^+) (BaCl(_2)) (meq/100g)</th>
<th>H(^+) (H(_2)O) (meq/100g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>0-30</td>
<td>5.5\times10^{-2}</td>
<td>8\times10^{-3}</td>
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<tr>
<td>12</td>
<td>30-60</td>
<td>4\times10^{-2}</td>
<td>1.4\times10^{-2}</td>
</tr>
<tr>
<td>13</td>
<td>60-90</td>
<td>3.9\times10^{-2}</td>
<td>7.2\times10^{-3}</td>
</tr>
<tr>
<td>14</td>
<td>90-120</td>
<td>2.7\times10^{-2}</td>
<td>1.35\times10^{-2}</td>
</tr>
<tr>
<td>15</td>
<td>150-180</td>
<td>3\times10^{-3}</td>
<td>8.2\times10^{-3}</td>
</tr>
<tr>
<td>16</td>
<td>210-240</td>
<td>1.9\times10^{-3}</td>
<td>1.2\times10^{-2}</td>
</tr>
<tr>
<td>17</td>
<td>270-300</td>
<td>3\times10^{-3}</td>
<td>1.1\times10^{-2}</td>
</tr>
<tr>
<td>18</td>
<td>360-390</td>
<td>8.4\times10^{-4}</td>
<td>4.5\times10^{-3}</td>
</tr>
<tr>
<td>19</td>
<td>420-440</td>
<td>1.4\times10^{-3}</td>
<td>6.3\times10^{-3}</td>
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<tr>
<td>20</td>
<td>450-480</td>
<td>8.9\times10^{-4}</td>
<td>6.1\times10^{-3}</td>
</tr>
</tbody>
</table>

### Chapter 3  Sorption of hydrophobic organic compounds (HOC).

#### Introduction

Tables for Chapter 3 may be found [at this link](#).

Hydrophobic organic compounds (HOC) are common contaminants in soils and sediments. HOC include aromatic compounds in petroleum and fuel residue, chlorinated compounds in commercial solvents and chemicals no longer produced in the United States, for example DDT (Luthy et al, 1997). For hydrophobic organic compounds, sorption is a critical process controlling the fate of these chemicals in groundwater. It is important to understand and be able to predict the transport and fate of HOC for choosing effective remediation procedures. Sandy glacial aquifers are an important source of groundwater. The Long Island sandy upper glacial aquifer is a typical example of glacial aquifer. The problem of HOC contamination of the sediments is especially important for Long Island, because most drinking water passes through this aquifer.

Hydrophobic organic compounds are exchanged between dissolved and sorbed phases in the subsurface. Water flows through aquifer sediments and dissolved HOC interacts with sediments and can be sorbed on the sediments (sorbent). The distribution coefficient (K\(_d\)) describes the distribution of HOC between water phase and surface of sediments.
sorbent for exchangeable cations. The soil complex in the top part enriched with Al ion (up to 82%) and contains minor amount of Ca (up to 8%). With depth amount Al and Ca drops. Concentration of H ion in both

Where $C_{\text{sediment}}$ is the concentration of HOC sorbed on the sediments and $C_{\text{water}}$ is the concentration of HOC in the water phase.

The $K_d$ is dominantly a function of the abundance organic matter of the solid ($f_{oc}$), (Schwazenbach et al, 1993).

$$K_d = C_{oc} * f_{oc} / C_w$$ (eq. 2)

Where $C_{oc}$ is the concentration of sorbate associated with organic carbon and $C_w$ is the concentration of non-polar organic compounds in solution (Schwazenbach, et al., 1993). The ratio of $C_{oc}$ to $C_w$ is the carbon normalized partitioning coefficient $K_{oc}$. The $K_{oc}$ describes the distribution or partitioning of HOC between two immiscible solutions (organic matter and water) (Schwazenbach et al,1993).

$$K_{oc} = C_{oc} / C_{ow}$$ (eq. 3)

Different studies in the literature provide the range of the predicted relationships between $K_{oc}$ and the compounds octanol-water coefficient ($K_{ow}$ is a measure of HOC hydrophobicity). Three equations, that represent the range of $K_{oc}$ predicted, were used to estimate the expected $K_{oc}$ for HCB.

$$\log K_{oc} = 0.82*\log K_{ow} + 0.44 \quad \text{(Schwazenbach et.al., 1993)}$$ (eq. 4)

$$\log K_{oc} = \log K_{ow} - 0.21 \quad \text{(Karicknoff et al., 1979)}$$ (eq. 5)

$$\log K_{oc} = 0.72*\log K_{ow} + 0.49 \quad \text{(Schwarzenbach and Westall, 1981)}$$ (eq. 6)

$K_d$ and $f_{oc}$ were measured during experiment and experimental $K_{oc}$ then was calculated.

$$K_d = K_{oc} * f_{oc} \Rightarrow K_{oc} = K_d / f_{oc}$$ (eq. 7)

Comparison of experimental and predicted $K_{oc}$ can give information about HOC sorption, and which sediments characteristics are mainly responsible for the sorption.

On the sediments with significant amount of organic matter, organic matter is mainly responsible for sorption of nonpolar organic compounds. In an environment with a very low fraction of organic matter ($f_{oc} \leq 0.0002$ - 0.001) association of HOC with mineral surface may be significant (Schwazenbach et al, 1993). Long Island sediments contain a low fraction of organic carbon. Possibly, both mechanisms: organic material and mineral surface sorption could be significant.

The rate of sorption of organic compounds on non-porous mineral surfaces is faster than rate of sorption on porous surfaces (Huang et al., 1996). Holmen and Gschwend (1997) suggest that the rate of the sorption is controlled by diffusion of HOC through the coatings. In this study we measured sorption after 48 hours (short term sorption). It has been shown that sorption equilibrium for HOC on sandy aquifer sorbents may take days to years (Ball and Roberts, 1991). The treatment of sediments (sonication e.t.c.) may have a significant effect onto both the availability of sorption sites and the kinetic approach to equilibrium.

In this study we want to determine the following: are coatings important in the sorption of HOC and what is
the relative importance organic carbon content and surface area in sorption of HOC in these sediments?

**Approach**

All sands, chosen for this experiment have coatings. A study conducted in Cape Cod, Massachusetts with aquifer sands similar to Long Island presented evidence that coatings are responsible for most HOC sorption, because the largest fraction of organic carbon concentrated in the coatings (Holmen and Gschwend, 1997).

For the HOC sorption study, four samples of sands from Long Island were chosen. All samples contained coatings on the grain surfaces. Samples 1 and 5 (from 100-120 and 160-180 cm below the surface) are medium-coarse sand from Port Jefferson. Samples 6 and 7 (from 140-150 and 200-220 cm below the surface) are medium-coarse and coarse sand from South Setauket (See methods). As a nonpolar hydrophobic organic compound, Hexachlorobenzene (HCB) was chosen, because of its high binding capacity (log Kow = 5.50). As a result sorption can be followed with a small amount of coatings and HCB is undegradable by microorganisms.

The distribution coefficient ($K_d$) was measured on: the whole coated sand, coatings separated by sonication, skeletal grains without coatings (naked sand), whole sonicated sand including coatings and HCl-treated sand including coatings but without iron compounds.

**Results**

The $K_d$ values for HCB sorption described with different samples and treatments are summarized in the Table 1 and Figure 1. The $K_d$ for whole sand varies between 2.5 ml/g (sample 7) to 10.7 ml/g (sample 1) (Table 1). The $K_d$ for coatings varies between 396 ml/g (coatings from sample 7) and 1480 ml/g (coatings from sample 1). The $K_d$ for the naked sand is always lower than that observed for the whole sand and the coatings varies between 1.55 ml/g (naked sand from sample 6) and 9.02 ml/g (naked sand from sample 5) (Table 1).

Figure 1. The comparison among the $K_d$ whole sand, the $K_d$ coatings, the $K_d$ naked sand, the $K_d$ sonicated sand but without separation of coatings, the $K_d$ HCl treated sand and the sum of $K_d$ coatings * fraction of coatings and $K_d$ of naked sand * f naked sand.
B. Sample 5. Medium-coarse sand from Port-Jefferson at depth 160-180 cm.

C. Sample 6. Coarse sand from Port-Jefferson at depth 120-140 cm.
D. Sample 7. Coarse sand from Port-Jefferson at depth 200-220 cm.

The $K_d$ for the sonicated sand (but without separation of the coatings) are always higher than that for un-sonicated whole sand were in the range 7.53 ml/g (sample 6) and 35.7 ml/g (sample 5). HCl treatment was done only for samples 1 and 5, and $K_d$ is 34.9 ml/g and 42.8 ml/g (Table 1).

The fraction of the coatings separated by sonication varies from 0.008 to 0.065 (Table 2). The $K_d$ of the whole sand was compared to that of the coatings and naked sand by using mass balance (Table 3).

$$K_d\text{ total} = K_d\text{ coatings} \times f_{\text{coatings}} + K_d\text{ naked sand} \times f_{\text{naked sand}}$$ (eq. 8)

The $K_d$ of the whole sand for all samples is always lower than $K_d$ for the whole, sonicated sand (Figure 1), showing that the process of sonication changes $K_d$ significantly. The $K_d$ following sonication of sample 1 was increased by 41.8%, sample 5 $K_d$ was increased by 20.1%, sample 6 $K_d$ was increased by 58.4%, and sample 7 $K_d$ was increased by 73.1% (Figure 1). Probably, sonication exposes or opens up pore space and HOC diffuses faster through the pore space and also the area available for sorption increases. For example, surface of cemented grains may become exposed. Therefore, more organic molecules can be sorbed in a shorter amount of time.

The removal of iron cement by HCl dissolution also increases $K_d$, consistent with explanation above. Iron compounds cement fine particles together and their dissolution opens up pore spaces.

For samples, which contain a higher fraction of coatings (samples 1 and 5), the $K_d$ for whole sonicated sand is...
always lower than the estimated $K_d$ (sum of coatings and naked sand $K_d$). For samples with a low fraction of coatings (samples 6 and 7) calculated whole sand $K_d$ is lower than the $K_d$ for sonicated whole sand. There are several possible explanations for why this is so. First, should be noted that the procedure for sonication varied in the experiments where coatings were separated and in these, in which sorption was measured into the whole sonicated sand. Most important, the separated coatings and naked sand were re-dried before sorption experiment, which may have affected aggregates stability. Another possibility is that sonication of grains with low fraction of coatings changes surface area and pore space in the large grains more significantly than with sonication of the samples with a high coatings fraction, which have a significant surface area available for sorption even without sonication. The mass-balance (Figure 1, Table 3) suggests that in all four samples the major amount of HOC sorbed could be attributed to the coatings. In sample 1, 85% of HOC sorbed on the coatings, in sample 5, 84.5%, in sample 6, 72.8%, in sample 7, 64.7%. Data suggests that the coatings could be the primary sorbent for hydrophobic contaminants like HCB.

Coatings contain chiefly clay minerals (illite, kaolinite and chlorite) with minor amounts of iron compounds and organic matter. For hydrophobic organic compounds, natural organic matter is often the main sorbent phase. Measurements of total organic carbon (TOC) on the whole sand and coatings show that the weight fraction of TOC varies on the whole sand from 0.0002 (sample 6) to 0.00027 (sample 1) (Table 4). TOC on the coatings displayed a wider range; from 0.0021 (sample 5) to 0.0076 (sample 1) (Table 4). TOC was estimated on the coatings by multiplying TOC on the whole sand by the fraction of the coatings (Table 4). The contribution of the coatings to the TOC of the whole sand was calculated as

$$f_{oc}(\text{coatings estimated}) = f_{oc}(\text{coatings}) \times f_{coatings}$$

(eq. 9)

For samples 1 and 5, the estimated TOC of the coatings contributes a large fraction of the TOC on the whole sand but for samples 6 and 7, the estimated TOC contribution from coatings is significantly lower than the TOC of the whole sand (Table 4). We assumed that some amount of TOC is associated with naked sand grains. TOC of the naked grains was calculated as the difference between the whole sand TOC and the estimated coatings TOC. Naked sand TOC for the samples with a low fraction of coatings (samples 6 and 7) is higher than for the samples with a high fraction of coatings (samples 1 and 5) (Table 4). Probably, coatings in samples 6 and 7 are harder to remove and coating residue is responsible for the high TOC on the naked sand skeletal grains. The comparison between the coatings $K_d$ and fraction of TOC indicates that samples with higher fraction of TOC have higher $K_d$. The exception is sample 5, which has the lowest fraction of TOC and the highest $K_d$ (Figure 2). We can hypothesize that the natural organic matter of the sediments was predominantly responsible for HCB sorption. Possibly in sample 5, along with fraction of TOC, other factors, for example surface area, may control sorption of HOC.
Surface area controls the sorption of HOC on the sediments with a very low fraction of organic carbon. Surface area measured on the whole sand has shown the following results: sample 5 has the highest surface area at 3.2 m²/g and sample 7 has the lowest, at 1.03 m²/g (Table 5). Whole sand with higher surface area has a higher $K_d$ value.

The coatings appear to be the major sorbent for HOC. Using a mass-balance 85%, 84.5%, 72.8% and 64.7% of the HCB sorption may be contributed by the coatings on the samples 1, 5, 6 and 7 respectively. According to Holmen and Gschwend (1997) the main sorption sites in aquifer sands for HOC occurs within coatings. They suggest this because the fraction of organic carbon on the coatings is higher than on the whole sand. Coatings are described as associations of natural organic matter with iron and aluminum-bearing minerals. Sand from the Pine Barrens (New Jersey), which Holmen and Gscwend used in their experiment, is chiefly quartz-covered with coatings composed of goethite, kaolinite and organic material. Coatings on Long Island sediments have similar composition: clay minerals (Illite, kaolinite and chlorite), organic matter and a minor amount of iron compounds.

The organic carbon normalized partition coefficient ($K_{oc}$) indicates an organic sorbate distributing itself between two immiscible solutions (organic matter and aqueous solution) (Scwazenbech, et al, 1993). The experimental partitioning coefficient $K_{oc}$ was calculated for HCB (Equation 7). The $K_d$ and the $f_{oc}$ were measured for each sample. The measured log $K_{oc}$ for the whole sand lies between 5.10 (sample 5) and 4.02 (sample 7). The log $K_{oc}$ for coatings lie between 5.52 (sample 5) and 5.06 (sample 7). The log $K_{oc}$ for naked sand lie between 5.05 (sample 1) and 3.98 (samples 6 and 7) (Table 6).

The calculation of predicted $K_{oc}$ values are presented in Table 6 and based on the following equations 4, 5 and 6. The $K_{oc}$ is the water-organic mater partitioning coefficient and $K_{ow}$ is octanol-water partitioning coefficient. Log $K_{ow}$ was determined for HCB and equaled 5.50 (Chiou et al., 1982). Predicted log $K_{oc}$ varied between 5.29 and 4.45.
Experimental log $K_{oc}$ for the whole sand is closer to the low predicted log $K_{oc}$ (the exception is sample 5, showing a high log $K_{oc} = 5.10$). Experimental log $K_{oc}$ for the coatings is closer to the high predicted log $K_{oc}$ (the exception is sample 5, showing a high log $K_{oc} = 5.52$ is higher than high predicted value). The experimental log $K_{oc}$ for the naked sand is closer to the low predicted log $K_{oc}$ (exception is sample 1 log $K_{oc} = 5.05$) (Table 6). High values log $K_{oc}$ for sample 5 may suggest that not only natural organic matter was responsible for sorption of HOC but also surface area (sample 5 has the lowest fraction of TOC and the highest whole sand surface area). The log $K_{oc}$ for the whole sand is generally lower than the predicted range of $K_{oc}$ (especially for samples 6 and 7) (Table 6). This may indicate that not all organic matter was available for sorption. Holmen and Gschwend (1997) observed that the column $K_d$ values were always much less than measured from batch testing and predicted values. They suggested that association of negatively charged organic matter molecules with positively charged iron oxide minerals formed aggregates, in which such organic matter may not be really available for sorption. During batch test disaggregation of these aggregates may expose organic matter and make them available for sorption. Probably, increasing $K_d$ value after sonication of the whole sand may be explained by the exposure of organic matter, which was unavailable for sorption before sonication. In the experiments with HCB, sorption kinetic limitation for pore diffusion may occur. The experiment was equilibrated for 48 hours (short-term sorption) which may not be sufficient to attain equilibria with less accessible organic matter. We could not do long term equilibria experiment because some leakage from bottles occurred. But it is also possible that some amount of organic matter would be totally unavailable for sorption regardless how long we waited for complete sorption. We concluded that natural organic matter of the soil was predominantly responsible for HCB sorption. This statement is questionable for sample 5, in which surface area may also be a significant factor in the sorption of HOC.

It has been argued that for low organic carbon sorbents like aquifer sands, the mineral surface adsorption of hydrophobic organic compounds becomes increasingly significant (Schwazenbach et al, 1993). A surface area normalized partitioning coefficient ($K_{sa}$, L/m$^2$) was calculated from our results and compared to $K_{sa}$ values measured for tetrachlorobenzene with various mineral surfaces (Table 7).

$$K_d = K_{sa} \times S.A.$$  \hspace{1cm} (eq. 10)

$$K_{sa} = K_d / S.A.$$  \hspace{1cm} (eq. 11)

where $K_d$ is the experimentally determined distribution coefficient (ml/g) and S.A. is surface area (m$^2$/g). The predicted $K_{sa}$ was calculated by using surface area (S.A) and mineral $K_d$ data from Table 11.3 in Schwazenbach, Gschwend and Imboden, (1993).

Porosity silica, g-alumina and kaolinite were chosen as sorbent. Given $K_d$ for tetrachlorobenzene were corrected by a factor of 10 because this study was done with HCB and HCB is about 10 times more hydrophobic than tetrachlorobenzene ($K_{ow}=4.50$). Schwazenbach et al, (1993) have shown that mineral surface sorption of different sorbates is almost directly proportional to $K_{ow}$ of sorbates. We understand that this may represent a rough approximation of $K_{sa}$ values, but should be useful for comparing the magnitude of $K_{sa}$ measured and those calculated for organic free minerals. The $K_{sa}$ estimated for pure minerals varies between 0.18 ml/m$^2$ (g-alumina) and 4.08 ml/m$^2$ (kaolinite). Experimental $K_{sa}$ values lies between 2.13ml/m$^2$ (sample 6) and 9.95 ml/m$^2$ (sample 5). Generally, the $K_{sa}$ predicted is lower than the $K_{sa}$ experimental. This result is consistent with hypothesis that the sorption of HOC was controlled mainly by the natural organic matter and less so by the surface area.

**Conclusions**
1. The $K_d$ values for HCB sorption on the coatings are much higher than those of the whole sand. The results suggest that sorption by the coatings likely contributes much of the short-term (24-48 hours) sorption of the whole sand.

2. Sorption of HCB by the coatings is consistent with the amount of organic matter on the coatings. The partitioning of HCB into the organic matter is likely to control sorption. However, some contribution of adsorption of HCB onto bare mineral surface is also possible.

3. Some amount of natural organic matter remains unavailable for sorption of HOC into sand particles during short-term (48 hours) sorption experiment. Possibly, during a longer sorption experiment more organic carbon may become available for sorption. The $K_{oc}$ predicted is higher than those experimentally determined on the whole and the naked sand samples.

4. Different treatments (sonication e.t.a.) affect the sorption capacity of the sand. First, sonication opens up pore space and diffusion of HOC to the sorption sites may occur faster. Second, a larger surface area exposed after sonication and become available for sorption. Third, more of the organic carbon may become available for sorption after sonication.

Tables for Chapter 3 - Sorption of hydrophobic organic compounds

Table 1. The $K_d$ values for the whole sand, the coatings, the naked sand, the sonicated sand but without separation of coatings and the sand without iron compounds. Samples 1 and 5 from Port Jefferson and samples 6 and 7 from South Setauket.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Whole sand</th>
<th>Coatings</th>
<th>Naked sand</th>
<th>Sonicated sand but without separation of coatings</th>
<th>Sand without iron compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10.7</td>
<td>1480</td>
<td>6.98</td>
<td>18.4</td>
<td>34.9</td>
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<tr>
<td>5</td>
<td>31.8</td>
<td>703</td>
<td>9.02</td>
<td>39.8</td>
<td>42.8</td>
</tr>
<tr>
<td>6</td>
<td>3.13</td>
<td>517</td>
<td>1.55</td>
<td>7.53</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>2.50</td>
<td>396</td>
<td>2.03</td>
<td>9.28</td>
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</tr>
</tbody>
</table>

Table 2. Fraction of the coatings to the whole coated sand mass. Medium-coarse coated sand from Port Jefferson (samples 1 and 5) and coarse sand from South Setauket (samples 6 and 7).
<table>
<thead>
<tr>
<th>sample</th>
<th>fraction of coatings</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.027</td>
</tr>
<tr>
<td>5</td>
<td>0.065</td>
</tr>
<tr>
<td>6</td>
<td>0.008</td>
</tr>
<tr>
<td>7</td>
<td>0.009</td>
</tr>
</tbody>
</table>

Table 3. The estimation of the contribution of the naked sand \( f_{\text{naked\ sand}} * K_d^{\text{naked\ sand}} \) and the coatings \( f_{\text{coatings}} * K_d^{\text{coatings}} \) to the sorption of the whole sand from Port Jefferson (samples 1 and 5) and South Setauket (samples 6 and 7).

<table>
<thead>
<tr>
<th>sample</th>
<th>Naked sand ( K_d ) (ml/g)</th>
<th>Coatings ( K_d ) (ml/g)</th>
<th>Total ( (naked\ sand+coatings) ) ( K_d ) (ml/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.80</td>
<td>39.5</td>
<td>46.3</td>
</tr>
<tr>
<td>5</td>
<td>8.43</td>
<td>45.9</td>
<td>54.3</td>
</tr>
<tr>
<td>6</td>
<td>1.53</td>
<td>4.1</td>
<td>5.63</td>
</tr>
<tr>
<td>7</td>
<td>2.01</td>
<td>3.69</td>
<td>5.70</td>
</tr>
</tbody>
</table>

Table 4. Fraction of organic carbon (TOC) measured on the whole sand, the coatings and the naked sand and estimated for the coatings. Coated medium-coarse sand from Port Jefferson (samples 1 and 5) and coated coarse sand from South Setauket (samples 6 and 7).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Whole sand ( f_{\text{oc}} )</th>
<th>Coatings ( f_{\text{oc}} )</th>
<th>Estimated for the coatings ( f_{\text{oc}} ) (equation 9)</th>
<th>Calculated for the naked sand ( f_{\text{oc}} ) (equation 9)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.00027</td>
<td>0.0076</td>
<td>0.00021</td>
<td>0.00006</td>
</tr>
<tr>
<td>5</td>
<td>0.00025</td>
<td>0.0021</td>
<td>0.00014</td>
<td>0.00011</td>
</tr>
<tr>
<td>6</td>
<td>0.00020</td>
<td>0.0045</td>
<td>3.56*10^{-5}</td>
<td>0.00016</td>
</tr>
<tr>
<td>7</td>
<td>0.00024</td>
<td>0.0028</td>
<td>2.6*10^{-5}</td>
<td>0.00021</td>
</tr>
</tbody>
</table>

Table 5. Surface area measured on the whole sand, the coatings and the surface area contribution that coatings make to the whole coated sand form Port Jefferson (samples 1 and 5) and South Setauket (samples 6 and 7).
### Table 6. The comparison among the log $K_{oc}$ whole sand, log $K_{oc}$ coatings, log $K_{oc}$ naked sand and predicted log $K_{oc}$. Samples 1 and 5 (Port Jefferson) and 6 and 7 (South Setauket).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Whole sand</th>
<th>Coatings</th>
<th>S.A. estimated whole sand = S.A. coatings * $f_{coatings}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.54</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>3.20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>1.47</td>
<td>18.8</td>
<td>0.15</td>
</tr>
<tr>
<td>7</td>
<td>1.03</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Table 7. The comparison between the experimental and the predicted $K_{sa}$ values for the whole sand. Samples 1 and 5 (Port Jefferson) and 6 and 7 (South Setauket). Surface area and $K_d$ for porous silica, alumina and kaolinite for calculation of predicted $K_{sa}$ were taken from (Schwazenbach, et al., 1993).

<table>
<thead>
<tr>
<th>Samples</th>
<th>$K_{sa}$ (ml/m²) Experimental (equation 10)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.22</td>
</tr>
<tr>
<td>5</td>
<td>9.95</td>
</tr>
<tr>
<td>6</td>
<td>2.13</td>
</tr>
<tr>
<td>7</td>
<td>2.42</td>
</tr>
<tr>
<td>Porous silica</td>
<td>0.24</td>
</tr>
<tr>
<td>g-Alumina</td>
<td>0.18</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>4.08</td>
</tr>
</tbody>
</table>
Chapter 4 Composition of the coatings.

Results

Most of the glacial sand on Long Island is composed of quartz that is covered with iron-stained coatings. The color of these coatings varies from bright orange-yellow to pale beige. In most cases, the proportion of coatings in the sediment determines the sorption capacity of the sediments, even though the coatings constitute only 0.8 to 13% of the sediment (Table 1), (Coston et. al, 1995). As a result, it was necessary to evaluate the mineralogical and the chemical composition of the coatings. Coarse and medium-coarse sand from Port Jefferson (samples 1 and 5) and South Setauket (samples 6 and 7) and fine sand from beach cliff at David Weld Preserve were chosen because these sediments contain a significant proportion of coatings and represent different depths and environments (see Methods).

The morphology of the grains surfaces and coatings of the whole untreated sand was examined by SEM. Transmission electron microscopy (TEM) was used to examine coating separates. Chemical analysis and selected-area electron diffraction (SAED) patterns of individual fine particles were collected to aid in mineral identification. The clay assemblage of the coatings was identified by X-ray diffraction (XRD). Also total organic carbon was measured (TOC) on both the whole sand and the coatings.

X-ray diffraction (XRD)

X-ray diffraction was used to distinguish the clay minerals in the < 2mm fraction of the fine coatings from fine sand at the beach cliff at David Weld Preserve (Figure 1 and Table 1).

Table 1. Basal Reflection d-spacings for common clay minerals.

<table>
<thead>
<tr>
<th>Clay</th>
<th>14 Å</th>
<th>10 Å</th>
<th>7 Å</th>
<th>5 Å</th>
<th>3.5-3.6 Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorite</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Kaolinite</td>
<td></td>
<td>X</td>
<td></td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Illite</td>
<td></td>
<td></td>
<td>X</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>Vermiculite</td>
<td>X</td>
<td>X</td>
<td></td>
<td>X</td>
<td></td>
</tr>
</tbody>
</table>

Illite is unambiguously recognized by the 10 Å and 5 Å reflection peaks. Chlorite has 14 Å, 7 Å, and 3.5 Å basal reflections, which coincide with basal reflections for kaolinite and vermiculite. An additional test was necessary to distinguish between the second chlorite reflection at 7 Å and the first kaolinite reflection at 7 Å using the procedure of Moore (1989). An aliquot of the sample was boiled for 2 hours in 6M HCl. Under these conditions most chlorite is dissolved and any residual 7 Å peak presumed to indicate kaolinite. In this sample the residual 7 Å peak was observed which indicates the presence of kaolinite (Figure 2 A). To distinguish between the 14 Å chlorite reflection and the 14 Å vermiculite reflection, the sample was heated at 300°C for an hour (Moore, 1989). This treatment collapses vermiculite to 10 Å, but chlorite retains its 14 Å peak. In this sample 14 Å peak is observed after heat treatment, which indicates the presence of chlorite (Figure 2 B). After heat treatment the 14 Å peak is smaller than the 10 Å peak suggesting that vermiculite or a mixed chlorite-
vermiculite may be present. Illite, kaolinite and chlorite are unambiguously present in this sample.

**Scanning Electron Microscopy (SEM)**

Scanning Electron Microscopy (SEM) was used to examine the surface of untreated medium-coarse sand from Port Jefferson (samples 1 and 5), and fine coated sand from the beach cliff at the David Weld Preserve (sample 10). SEM examination was done to evaluate whether the morphology of the particles in the coatings could clarify whether the particles are authigenic or detrital.

The surface of the quartz grains are extensively covered with fine particles of the different sizes and shapes (Figures 3, 4, 5, 6 and 9). The images of the medium-coarse sand from sample 1 are shown in the Figures 3, 4, 5, 6, 7, and 8. The SEM images of the fine coated sand from sample 5 are shown in Figures 9 and 10. The SEM images of sample 10 are shown on the Figures 11 and 12.

Most particles have irregular shapes. Almost all quartz grain surfaces are covered with coatings (Figures 5 and 9). The uncoated areas of quartz show signs of extensive weathering (etch pits) (Tazaki, Fyfe, 1986) (Figure 8). Within the coatings the smaller particles are observed to be on the surfaces of larger particles (Figures 5 and 6). Grains with laminar structure are observed in Figure 11. In sample 5 (coarse-medium sand from Port Jefferson) platy grains, possibly clay particles, were noticed (Figures 9 and 10). Pseudo-hexagonal crystals were identified in sample 5 (Figure 10). This may be the evidence of authigenic clay (Tazaki, Fyfe, Van der Gaast, 1989; Small 1992). Except for this sample most of the grains have irregular shapes.

The fine sand from the beach cliff at the David Weld Preserve contains a significant fraction of mica shaped grains and grains with platelet morphology (Figure 11).

**Transmission Electron Microscopy (TEM)**

Transmission electron microscopy was undertaken to determine the mineralogy and composition of the coating particles. Ultrasonically separated coatings from sample 1 (coarse-medium sand from Port Jefferson) were chosen because this sample is heavily covered with a bright brown-orange colored coating. The TEM images are shown on the Figures 13A, 13B, 13C, and 13D.

The coatings contain particles of different sizes. Figure 13A shows a large grain 3 to 4 mm in size. The dark grain in the upper right corner is almost 1 mm. The smaller particles on the surface of the large grain vary in size from 1.2 mm (the largest one) to the less than 1/10 mm. A lot of very small particles are around the large grain, most of them form aggregates less than 1 mm. The largest grain in Figure 13C is 2.5 mm long and 1 mm wide. A lot of very small particles (sizes much less than 1 mm) are in the right low corner. Some small particles form aggregates, which are hard to distinguish from the individual grains. Most of the particles are platelets, consistent with layered silicates, but show irregular shape. Small particles are observed on the surface of the larger grains and around them (Figures 13A and 13C).

Selected-area electron diffraction (SAED) patterns of the individual grains were obtained to identify the mineralogy of the particles. The dispersed grain technique used for sample preparation results in a unique orientation of platy grains. Because of the strong preferred orientation of the platelet, all SAED patterns revealed dominantly a single zone-axis orientation of reciprocal space, i.e. the a-b plane. The large isolated grains give single-crystal spot patterns, whereas the aggregates of very small grains give ring patterns (Figures 13B and 13D). Essentially all particles showed diffraction contrast and indicating that all grains are crystalline.
The diffraction patterns were indexed using an independently calibrated camera constant $lL$ and the relationship

$$ R^*d = lL $$  \hspace{1cm} (eq. 1)

Where $R$ is the magnitude of the diffraction vector measured at the film, and $d$ is the interplater spacing. All particles have a 4.2-4.4 Å spacing for the a-b plane. The ring patterns of the aggregated small grains are superimposed on the spots. This indicates the similarity of crystal structure of the small particles and the large isolated grains. This spacing is characteristic of the clay minerals, kaolinite, smectite and illite. To distinguish among these clay minerals we need to rely on chemical analysis of the individual grains and the aggregates.

Chemical analyses of the individual grains and the particles aggregates were obtained by TEM. 1000 Å beam size was used for chemical analyses, this is 10 times smaller than the beam typically used in an electron microprobe. We were only able to analyze chemical composition of the large grains; for the small particles this beam size was too large as a result it was necessary to analyze aggregates of the finer particles.

The integrated intensities of the characteristic peaks for the different elements were measured. The peak intensities were converted to concentration using procedure introduced by Cliff and Lorimer (1975). The chemical compositions of the individual grains in the sample 1 are plotted on a ternary diagram (Figure 14) along with the compositional range of illite, chlorite, kaolinite, montmorillonite and celadonite. Except for kaolinite these clay minerals show broad compositional variability. The compositional range data of these minerals were taken from Newman (1987). Ternary diagram was constructed using molar ratios of K, Al and Fe+Mg to Si.

Figure 14. Ternary diagram shows compositional range for the fields of illite, chlorite, montmorillonite, kaolinite and celadonite and chemical composition of the coatings from sample 1 (red dots). The ternary plot is
constructed based on the molar K, Al and Mg+Fe to Si molar ratios.

The coatings are composed predominantly of Si, Al, with some Fe, K and Mg and minor amounts of Mn and Ca. Most of analyses plot close to illite, some are close to chlorite (Figure 14). Some spread in data was observed it might be due to the analytical uncertainty (5%) or variations in the chemical composition of the particles. The low number of counts is the main source of uncertainty. The measurement of the k-factor contributes to the uncertainty, but it was determined using the same procedure as the sample.

Results of the TEM examinations show that coatings have a large range of grain sizes, and in most cases irregular shape. Small and large particles have identical SAED patterns (4.2-4.4 Å). The TEM data as well as the XRD data suggest that the clay minerals are kaolinite, illite and chlorite.

**Total Organic Carbon (TOC)**

It is important to determine the content of organic matter in sediment because organic matter has high cation exchange capacity (200-400 meq/100g), (Appolo, 1992) and is the major sorbent for hydrophobic organic compounds (HOC). The weight fraction of TOC of whole sand varies between 0.0002-0.0003 (Table 2). Coatings have an order of magnitude higher fractions of TOC varying from 0.002 (coarse, heavily coated sand from Port Jefferson, sample 5) to 0.008 (coarse-medium sand from Port Jefferson, sample 1). The natural organic matter is typically made up of about half carbon so the fraction of organic carbon can be converted to fraction of organic matter by multiplying by 2 (Schwarzenbach et al, 1993).

\[ f_{om} = f_{oc} \times 2 \]  

(eq. 2)

Where \( f_{om} \) is fraction of organic matter and \( f_{oc} \) is fraction of organic carbon.

According to Schwazenbach et al (1993) Long Island sand contains relatively small fraction of organic carbon (\( f_{oc} = 0.0002-0.003 \)).

**Table 2.** Fraction of the coatings to the whole sand mass and fraction of total organic carbon (\( f_{oc} \)) measured on the whole sand and coatings. Sample 1 is coarse heavily coated sand from Port Jefferson (depth 100-120 cm below the surface). Sample 5 is medium-coarse sand from Port Jefferson (depth 160-180 cm below the surface). Sample 6 is medium-coarse sand from South Setauket (140-150 cm below the surface). Sample 7 is coarse sand (200-220 cm below the surface) from South Setauket.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Fraction of the coatings</th>
<th>Fraction of total organic carbon (( f_{oc} )) Whole sand</th>
<th>Fraction of total organic carbon (( f_{oc} )) Coatings</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.027</td>
<td>0.0003</td>
<td>0.008</td>
</tr>
<tr>
<td>5</td>
<td>0.065</td>
<td>0.0003</td>
<td>0.002</td>
</tr>
<tr>
<td>6</td>
<td>0.008</td>
<td>0.0002</td>
<td>0.005</td>
</tr>
<tr>
<td>7</td>
<td>0.009</td>
<td>0.0002</td>
<td>0.003</td>
</tr>
</tbody>
</table>
TEM, SEM and XRD analyses show that the coatings consist dominantly of illite, with minor kaolinite and chlorite. The particles in the coating material have a large range in grain sizes and shapes. The SAED analyses show that the large and fine particles all have identical diffraction patterns consistent with illite or kaolinite. Only very minor fractions of organic matter and iron compounds were identified in the coatings.

The Long Island stratigraphic sequence consists of highly weathered basement gneisses, schists and granites overlain by Cretaceous sands and clays of the Raritan and Magothy formations which are in turn overlain by glacial sediments (Sirkin, 1995). Significant fractions of the underlying Cretaceous sediments were picked up by the Wisconsinan glaciers and were incorporated in the upper glacial sediments (Sirkin, 1995).

Liebling and Scherp (1975) found kaolinite and illite present in all cores in the Cretaceous Raritan Formation on Long Island. They found kaolinite to be generally more abundant with chlorite making up one tenth to one third of the clay. Wakeland (1979) reported that Long Island clays are dominated by illite with lesser amounts of smectite, chlorite and kaolinite. Liebling (1973) found that kaolinite and illite were the dominant clays in the weathered bedrock samples from the northern part of Nassau County with minor amounts of intrastratified vermiculite-montmorillonite.

There are several studies of the mineralogy of the particles in coatings of glacial sediments in environments similar to those on Long Island. The following two studies were conducted on Cape Cod, Massachusetts. Wood et al., (1990) found a clay assemblage of illite (25%), kaolinite (25%) and smectite (3%) in coatings on glacial sediments on the southern border of Otis Air Base, Cape Cod, Massachusetts.

Coston et al., (1995) found that the glacial sand in Falmouth, Cape Cod, Massachusetts consists primarily of quartz (95%) with minor amounts of feldspar and ferromagnetic minerals. They also report that the particles in the coatings consist of a variable mixture of Fe oxides, smectite and polycrystalline material enriched in Al, Fe and Si. They proposed that most of the particles in the coatings were derived by weathering of feldspar and accessory minerals in the sediments.

Ryan and Gschwend (1992) studied an unconfined sandy aquifer composed mostly of coated sand in the Lebanon State Forest (central New Jersey). They suggest that coatings were formed as the result of the illuviation or "mechanical infiltration" of clay colloids particles of authigenic clay particles. However, an aluminous-rich mineral as a source for authigenic clay, for example feldspar is not abundant in the Cohanseay Sand.

In this study we found the clay mineral assemblage of the coating particles to be similar to the clay assemblage in the Cretaceous sediments. Therefore, the Cretaceous sediments could be the main source of clay minerals in the coating on Long Island. Exactly how the particles would be attached to the sand and silt grains is not clear.

We called "coatings" all fine grained material available after 30 minutes of sonication of coated sand or silt. After sonication the quartz grains lost most of their reddish-brown color. However, some fraction of strongly bonded material may be still left on the surface. Also, the material called coatings contains some fraction of fine particles not bonded to the mineral surface but which just filled the space between grains. It is not clear how one could sample the fine-grained interstitial material without including the particles in the coatings.

Did the particles in the coatings on the glacial sediments form before or after glacial deposition? The particles have irregular shapes and vary in size, which may be evidence for the physical crushing of the particles during
glacial transportation or deposition. The uncoated surfaces of quartz have etch pits. These etch pits could have formed during weathering of the source rock or sediments or after these sediments were redeposited by the glacier. Only one pseudo-hexagonal crystal was identified by SEM. This may be evidence for authigenic clay growth. If so, some clay may have formed authigenically. The data, which we have, are not sufficient to determine whether the clays have an authigenic or detrital origin.

References


Huang W., Schlautman and Weber W. A distributed reactivity model for sorption by soil and sediments. S.


Jackson M. Soil chemical analysis. Advanced course, 1974, p.335.


Mayer L. Surface area control of organic carbon accumulation in continental shelf sediments. Geochemica et


Young T. and Weber W. A distributed reactivity model for sorption by soils and sediments. 3. Effect of diagenetic processes on sorption energetics.