

FTIR Investigation of Sediments from NY/NJ Harbor, San Diego Bay, and the Venetian Lagoon

Z. Song^{1,4}, E. Chouparova¹, K.W. Jones¹, H. Feng², and N.S. Marinkovic³

¹Brookhaven National Laboratory

²Montclair State University

³Albert Einstein College of Medicine

⁴Guangzhou Institute of Geochemistry, Guangzhou, China

Introduction

Sediments found in rivers, estuaries, and marine environments in the United States are widely contaminated with both organic and inorganic compounds that have adverse effects on the environment and on human health. It is often necessary to dredge these materials for remedial reasons and/or to create or maintain navigational channels. In many cases it is impossible to directly dispose of the dredged materials in an aquatic location because of the potential harm to the environment so that other disposal methods must be developed.

The NY/NJ Harbor is an example of a contaminated urban estuary. Sediments are widely contaminated as a result of several hundred years of industrial activity in the watershed area and around the Harbor proper. The Harbor is the location of the largest port on the east coast of the United States. However, it is shallow with an average depth of less than 7 meters. Dredging is an absolute necessity to provide navigational channels that can be used by deep-draft container ships and other modern vessels, which require depths of 15 to 20 m. This maintenance dredging generates a dredged material volume of 2,000,000 m³ or more each year. Of this amount, approximately 75% is not suitable for ocean disposal and must be sent to upland disposal sites or employed as a material for beneficial use applications. The situation in NY/NJ Harbor is not unique. In fact, conceptually similar problems exist in the Great Lakes, Puget Sound, Galveston, Boston, and other locations in the United States. In addition, other countries and regions around the world are affected, for example, Italy, Norway, Germany, Holland, China, and Taiwan.

Thus, dredging of contaminated sediment is a routine requirement for efficient harbor operation. Processing these contaminated sediments so that they are environmentally harmless and suitable for beneficial use as a soil or cement or some other material, is aided by knowledge of the nature and distribution of organic contaminants in the sediments.

Our approach to selection of samples was based on the fact that natural sedimentary organic matter is

derived from various living organisms. Once these organic compounds are deposited in the sediments, they are immediately subject to the biochemical and geochemical transformation processes that occur in the changing sedimentary environment. The early stages of organic matter transformation (i.e. early diagenesis in geological term) involve humification (humic substance formation) and kerogen formation (kerogens are the organic materials found in sedimentary rocks). Then, further thermodynamic and geochemical influences transform the kerogen macromolecules into petroleum hydrocarbons (catagenesis). The chemical structure of organic matter at each stage is very different from the others. Therefore, if modern sediments display an unusual pattern of chemical structure, the sedimentary organic compounds must be of anthropogenic (human) origin. This is the basis for identifying and characterizing contaminated sediments.

Objectives

There are two objectives in this study: The first is to characterize the nature of organic materials in contaminated and uncontaminated sediments to help establish a model that can be used as a guide for differentiating between them. The second is to provide useful information about the basic types and abundance of organic contaminants in sediments that will be useful in devising improved methods for their destruction or removal.

Experimental Apparatus

The Synchrotron Fourier Transform Infrared (S-FTIR) experiments were carried out on the U2B beam line at the National Synchrotron Light Source. The beam line is equipped with a commercial Fourier Transform Infrared Spectrometer (Nicolet Magna 860) with a KBr beam splitter and MCT (Hg-Cd-Te) detector coupled with an infrared (IR) microscope (Nicolet NicPlan). Fourier Transform Infrared - Attenuated Total Reflectance (FTIR-ATR) was performed on a conventional Nicolet 560 FTIR spectrometer coupled with an ATR sampling device (International Crystal Labora-

tories). The spectra collected at the ATR apparatus were corrected for the wavelength-dependent path-length (ATR correction).

Results

We first measured the FTIR-ATR spectra of natural materials: Suwannee River and Nordic Aquatic humic and fulvic acid standards and three ancient kerogen samples from China. The spectra for humic acids, kerogens, and natural marine sediments are compared in Figure 1. The spectra of humic acid is characterized by broad and strong absorption in the 3000-3500 cm^{-1} interval (O-H and N-H stretching vibrations) and mod-

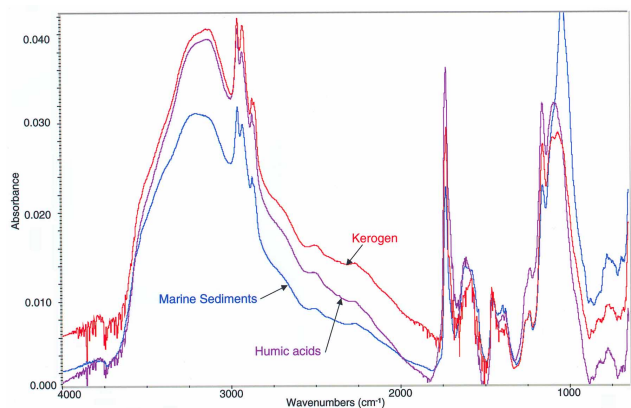


Figure 1. FTIR-ATR spectra comparison of humic acids, kerogen and normal marine sediments.

erate C-H stretching bands in the interval from 2800 to 2960 cm^{-1} . A strong C=O band at 1730 cm^{-1} and a group of C-O absorption peaks in the frequency range 1430-1050 cm^{-1} are also visible. A similar spectrum is observed for fulvic acid (not shown). The ancient kerogens display somewhat weaker C=O stretching vibrations, whereas the overall C-O stretch region is similar to that observed for the humic acid spectrum. The spectrum found for the marine sediments is generally similar to the spectra for the humic acid and kerogen.

The FTIR-ATR spectrum of uncontaminated clay sediments from the Venice Lagoon, Italy, taken from a depth of 4-4.7m is shown in Figure 2A. The estimated deposition time is about ten thousands years ago. This spectrum mainly shows the features of clay minerals and indicates that there is little organic matter in the sediments. Thus, this sediment was either originally lacking in organic matter or was deposited in a very oxidizing environment where freshly deposited organic matter was quickly decomposed.

Measurements were also made on sediments obtained close to the sediment surface at a site in San Diego Bay where minimal contamination is expected.

The spectra shown in Figure 2B were obtained from material taken at 0-4, 16-18, and 30-35 cm below the surface. The spectra are similar to those found for humic and fulvic acids (see Fig.1) indicating that the sedimentary organic matter is dominated by natural biochemical and geochemical products such as aldehydes, ketones, carboxylic acids, phenols, esters and amines.

As their sources would have suggested, organic matter in these modern and ancient sedimentary and aquatic environments is basically from autogenic sources and was little influenced by human activities. Therefore, the above spectra can be considered as models for the typical organic matter found in related

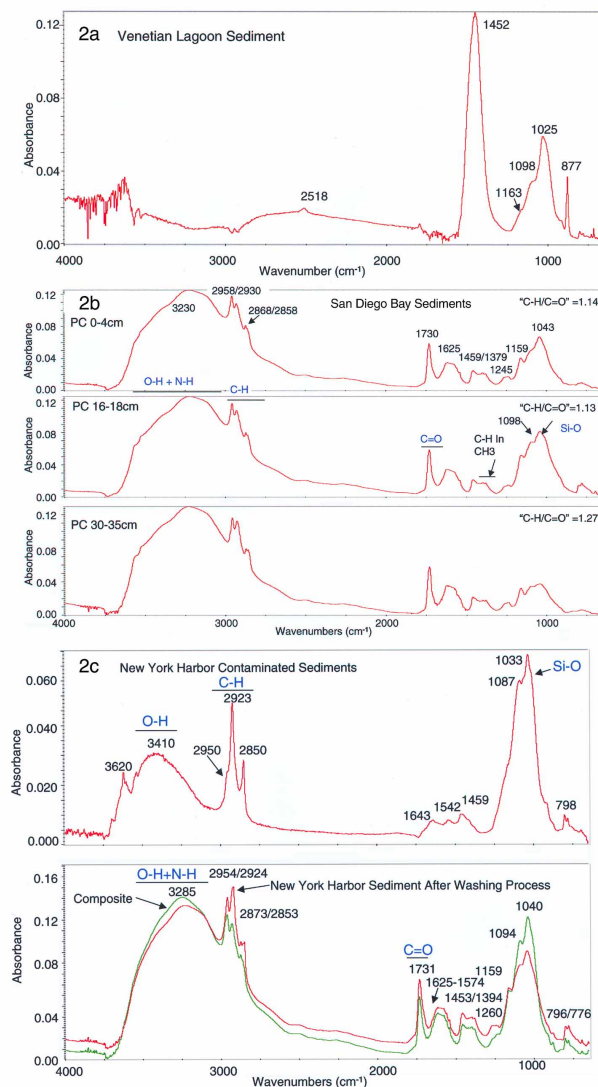


Figure 2. (a) FTIR-ATR spectra of uncontaminated clay sediments from Venice Lagoon, Italy, taken at the depth of 4-4.7m. (b) FTIR-ATR spectra of San Diego Bay sediments taken at different depths from a short core sample. (c) FTIR-ATR spectra of surficial contaminated sediments, a composite sediment, and a cleaned sediment from New York harbor.

natural or unpolluted sediments and other environmental systems.

Sediments from NY/NJ Harbor are an excellent example of sediments that have been heavily contaminated with organic materials of anthropogenic origin. The FTIR-ATR spectra for specimens taken from northern Newark Bay are shown in Figure 2C. Spectra are shown for as-sampled sediments taken from the sediment surface, for sediments taken from a core sample, and for a sample taken following treatment with a sediment washing process (BioGenesis Enterprises, Oak Creek, WI). The top figure shows the FTIR spectrum for the surficial sample. The bottom figure shows a spectrum for the homogenized material that is less contaminated (green) and the contaminated sediment that has gone through the sediment washing process (red). The contaminated sediments are characterized by very strong C-H stretching bands associated with longer chain aliphatic hydrocarbons. The cleaned sediment sample and the homogenized raw-core sediment sample from the same sampling site displayed much weaker C-H absorption bands and give spectra that are closely matched with the San Diego Bay spectra shown in Figure 2B. This suggests that the hydrocarbon abundance was much lower in the homogenized specimen, i.e. significant amounts of hydrocarbons have been destroyed or removed from the sediments during the cleaning process. However, the relatively higher proportion of C-H absorption peaks compared to the San Diego Bay spectra implies that a fraction of the aliphatic hydrocarbons may have been integrated into the humic acid-like organic complex.

The results of the spectral investigations are summarized in Table 1. Values for relative intensities of several functional groups are given for the different types of samples investigated. It appears that these values can be used as a general analytical tool in assessing the origins of the organic materials.

It can be seen that the use of ordinary laboratory FTIR instrumentation yields valuable insights into the nature of the materials investigated. The U2B FTIR microscope with the synchrotron beam as the IR source (S-FTIR) is, however, essential for mapping variability on a micrometer size scale. We used this capability to map the distribution of organic compounds extracted from the NY/NJ Harbor sediments using a water/methanol solvent. The liquid extracts were evaporated to dryness and examined at U2B. Figures 3 and 4 show the optical images of a colorless crystal found in the

extract, together with their FTIR representation. The size of the crystal (about 0.2 mm in diameter) prevents the analysis by the laboratory FTIR instruments. By taking an IR spectrum at 0.015 mm intervals across the entire crystal, using the IR microscope coupled with the synchrotron light as the source, a map is obtained that displays the intensity of the integrated band area in a certain frequency range. Figure 3 shows the spectrum of a 0.15 x 0.15 mm area located at the edge of the crystal (see arrow), the IR integrated intensity of the O-H stretching region, and the 3D representation of the map. The great variation of the infrared spectra and the non-uniformity by color within the optical scan area are evidence that the matter in this contaminated sediment is inhomogeneous, and/or the thickness of the crystal varies. If the S-FTIR data of the same crystal is processed for the C-H stretching region, a different map is obtained (Figure 4). The image map in Fig.4 shows that the C-H stretch is very intense, indicating the existence of a large quantity of aliphatic hydrocarbons in agreement with the spectrum obtained by FTIR-ATR for this sediment. Furthermore, the 3060 cm⁻¹ absorption peak confirms the presence of polycyclic aromatic hydrocarbons (PAHs). Therefore, these synchrotron FTIR images indicate that the extracts from these sediments are composed of various organic contaminants, mainly aliphatic hydrocarbons, nitrogen-containing compounds, as well as PAHs.

Table 1. Relative Abundances of Functional Groups

Samples	C-H/C=O	C-H/O-H	Identification
NY/NJ Harbor Sediments		0.19	Heavily contaminated sediments
NY/NJ Harbor sediments cleaned by sediment washing technology	2.33	0.048	BioGenesis proprietary technology
NY/NJ Harbor composite sample	1.87	0.028	
San Diego Bay Sediments 0-4 cm	1.44	0.028	Natural marine sediments
San Diego Bay Sediments 16-18 cm	1.35	0.029	
San Diego Bay Sediments 30-35 cm	1.47	0.026	
Suwannee River Humic Substance	0.17	0.01	Natural organic matter in river and other aquatic systems
Suwannee River Humic Acids	0.81	0.026	
Nordic Aquatic Humic Acids	0.60	0.028	
Suwannee River Fulvic Acids	0.54	0.037	
Nordic Aquatic Fulvic Acids	0.6	0.041	
FS Kerogen, China	2.24	0.042	Biochemical and geochemical altered sedimentary organic matter (ancient times)
HD Kerogen, China	1.96	0.032	
LN Kerogen, China	1.96	0.035	

The indication that the above compounds are of anthropogenic origin can be inferred by observing the differences in the spectra of the extracted organic material from contaminated sediments (Figs. 3 and 4), and that of natural (uncontaminated) sediments (Figs. 2A and 2B). However, a more direct proof of the origin of the contaminants can be inferred from the spatial distribution of the C-H and O-H functional groups (Figs. 3 and 4). The integrated intensity of the C-H region (Fig. 4) is a maximum at the edge of the crystal, whereas that of the O-H region (Figure 3) has its maximum predominantly deeper in the crystal. The difference in the spatial distribution of the two functional groups is a clear indication that contaminants are in fact of anthropogenic origin, because the aliphatic C-H bands, found in petroleum-based contaminants, occlude the crystal after it has been formed. In addition, the spectrum indicates that this crystal may contain an amine functional group, visible as a broad absorption in the 3500 – 3200 cm^{-1} range, that overlaps with the OH absorption region, and may represent a molecular complex. Finally, the fact that none of these spectra are similar to those found for uncontaminated sediments is noteworthy.

Conclusions

1. Natural sedimentary organic matter of humic acids, fulvic acids, ancient kerogen, and modern marine sediments are dominated by humic acid-like structures in the FTIR spectra but differ from each other in the relative abundance of functional groups.

2. NY/NJ Harbor sediments are contaminated by various organic compounds, mostly aliphatic hydrocarbons and possibly some nitrogen containing materials - with a small portion of PAHs. Thus, contaminated sediments can be clearly identified and characterized by using FTIR techniques.

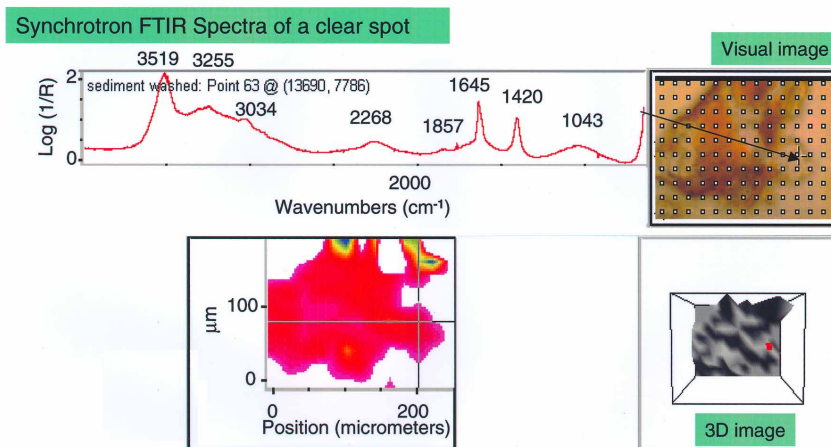


Figure 3. Optical image of a colorless crystal extracted from contaminated NY/NJ Harbor sediment (top right), S-FTIR spectrum of a 0.15 x 0.15 mm area shown by the arrow at the optical image (top left), and processed S-FTIR spectra at each point area showing the spatial distribution of the O-H stretching bands in 3600-3300 cm^{-1} frequency range in 2D (bottom left) and 3D (bottom right) view.

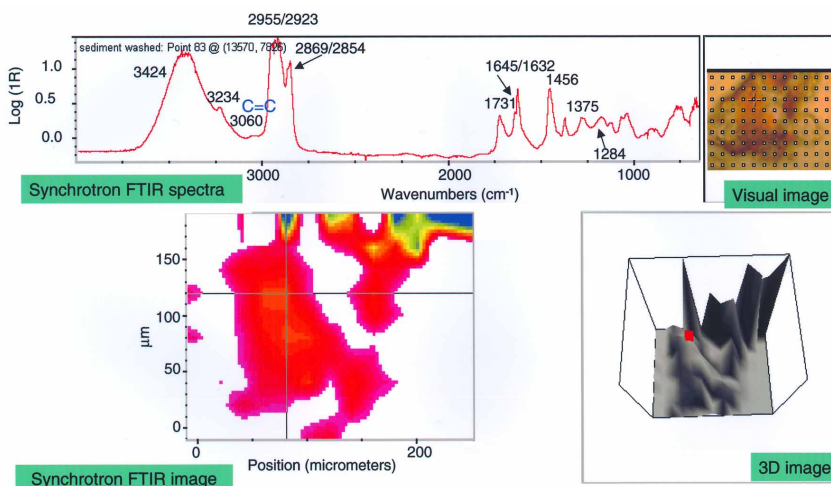


Figure 4. Optical image of a colorless crystal extracted from contaminated NY/NJ Harbor sediment (top right), S-FTIR spectrum of a 0.15 x 0.15 mm area shown by the arrow at the optical image (top left), and processed S-FTIR spectra at each point area showing the spatial distribution of the C-H stretching bands in 3000-2800 cm^{-1} frequency range in 2D (bottom left) and 3D (bottom right) view.

3. The effectiveness of sediment washing (BioGenesis Enterprises) technology for removing organic contaminants was shown. However, parts of the organic contaminants, namely aliphatic hydrocarbons, may have been integrated through biochemical and geochemical processes into humic acid-like organic complexes that give these materials a relatively high proportion of aliphatic functional group content.

4. The use of synchrotron IR microscopy provides very useful information on the spatial variation of the functional groups and organic components throughout a small section of the sediment, and demonstrates how micrometer-scale maps can help in identification of the origin of the contaminants.

Future Work

Although this work has established a general model for these contaminated and uncontaminated sediments based on their infrared absorption features, we still need to know the exact types and amount of organic contaminants, as well as the nature of the interaction of these contaminants with the natural organic matter and sediment particles. To clearly characterize the chemi-

cal properties and source of these organic contaminants the characterization of the water-soluble, organic-solvent-soluble, and the insoluble organic matter fractions in the sediments are necessary, as well as their distributions as a function of sediment particle size. The use of high-resolution synchrotron FTIR techniques is an essential tool for executing these investigations.

Acknowledgements

Research carried out in part at the National Synchrotron Light Source, Brookhaven National Laboratory, which is supported by the U.S. Department of Energy, Division of Materials Sciences and Division of Chemical Sciences, under Contract No. DE-AC02-98CH10886. Other aspects of the work were also supported by the U. S. Department of Energy, Division of Chemical Sciences, under Contract No. DE-AC01-98CH10886 and through Interagency Agreement DW89941761-01 between the U.S. Environmental Protection Agency and the U.S. Department of Energy. NSLS beamline U2B is supported by Grant No. RR-01633 from the US National Institutes of Health.