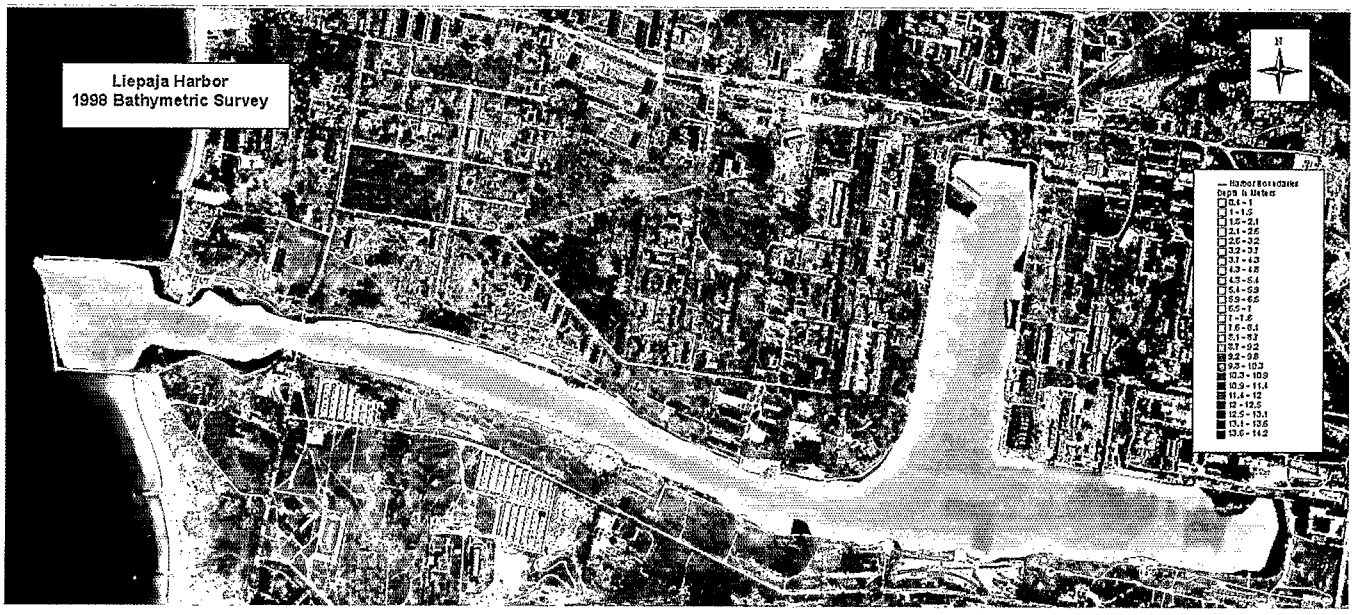
Assessment, Remediation and Management of Contaminated Sediments and Dredged Materials Workshop



Jurmala, Latvia
September 24-27, 2002

Sponsored by:

Latvian EPA

United States Environmental Protection Agency

Ministry of the Environmental Protection and Regional Development of the Republic of Latvia

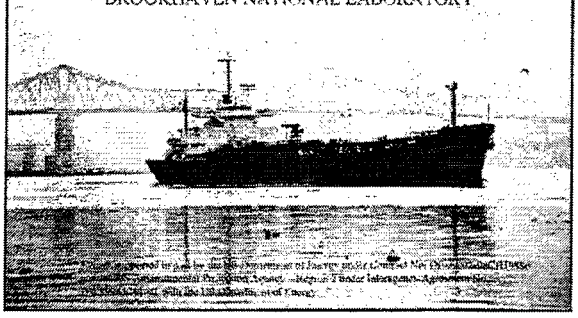
University of Latvia Institute for Marine Ecology

EPA

FIELDS
FIELD ENVIRONMENTAL DECISION SUPPORT

SEDIMENT SCIENCE AND ENGINEERING STUDIES

K. W. JONES
BROOKHAVEN NATIONAL LABORATORY



WHY IS SEDIMENT SCIENCE OF INTEREST?

- Record of geological processes and industrial activities
  - Subtleties of Sand Reveal How Mountains Crumble. Science 295, 256-258 (2002).
  - Sedimentary rock structures
- Sedimentary processes are a precursor to petroleum formation
- Methane hydrate recovery
- **Sediment contamination presents environmental problems**
- Biogeochemical transformations. See rationale given in US NSF call for proposals on Biogeochemistry: http://www.nsf.gov/cgi-bin/getpub?nsf02172

SEDIMENT-RELATED SCIENCE: INVESTIGATIONS RELATED TO NY/NJ HARBOR SEDIMENTS*

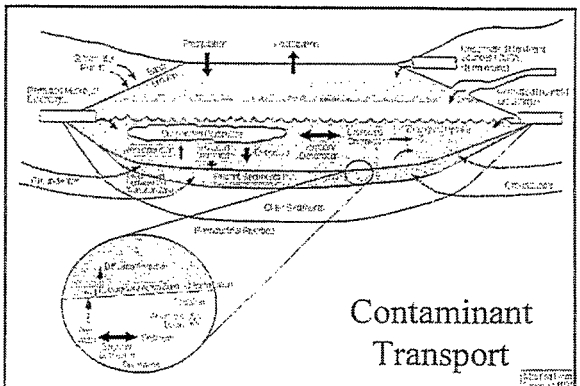
K. W. Jones

Laboratory for Earth and Environmental Sciences
Brookhaven National Laboratory

Presented at:
"Assessment, Remediation, and Management of Contaminated Sediments and Dredged Material Workshop
Jurmala, Latvia

25-27 September, 2002

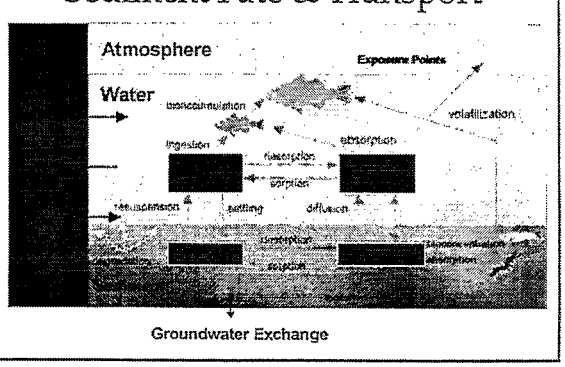
*Work supported in part by the US Department of Energy under Contract No. DE-AC02-98CH10886 and the US Environmental Protection Agency – Region 2 under Interagency Agreement No DW89941751-01 with the US Department of Energy.



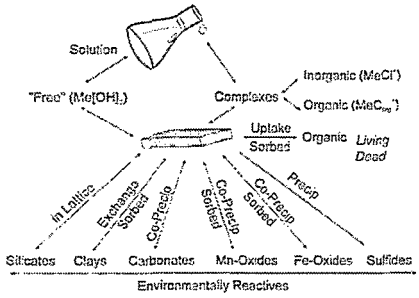
CO-WORKERS:

A. Lanzirotti, University of Chicago
Huan Feng, BNL, Montclair State University
Elli Tchouparova, BNL, Shell R&D Center
Zhiguang Song, BNL, Guangzhou Institute of Geochemistry
Sheng-rong Song, BNL, Taiwan National University
Nebojosa Marinkovic, Albert Einstein College of Medicine
Xu Sulan, Lore Barbier, Hong Ma, Michael, John Spiletic, Gordon Smith, Robert Marr, Graham Smith, Neils Van der Lelie, BNL
Ulrich Neuhäusler, ESRF
L. Vincze, B. Vekemans, K. Janssens, R. Van Grieken, F. Adams, University of Antwerp
I. Szalóki, University of Debrecen
Scott Douglas, New Jersey Office of Maritime Resources
E. A. Stern, U.S. Environmental Protection Agency – Region2

Sediment Fate & Transport



FATE OF METALS IN THE ENVIRONMENT



USEFUL WEB SITES FOR MODELING AND VISUALIZATION

Information on the US EPA 3MRA model can be found at:
http://www.epa.gov/athens/research/projects/3mra/index.html

US EPA FIELDS. Program with GIS, GPS, and 3-d visualization:
http://www.epa.gov/region5fields/

A compendium of visualization sites:
http://scv.bu.edu/SCV/hotlist.html Boston University List

GRASS is an open-source Geographic Information System:
http://www.geog.uni-hannover.de/grass/

OPENDX is an open-source visualization program:
http://www.opendx.org/

MODELING ACTIVITIES

Models are needed to make predictions about contaminant transport and fate in sediments and soils. They need to incorporate data taken at a variety of size scales.

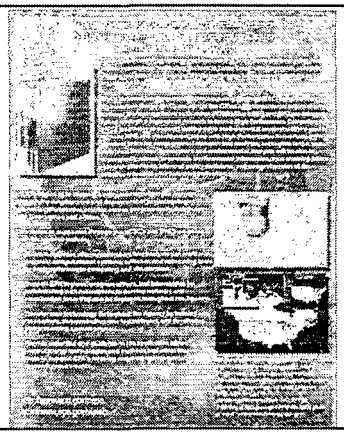
The US EPA model is the **"Multi-media, multi-pathway, multi-receptor exposure and risk assessment (3MRA)"** open-architecture model.

New directions: 1. science support research activities focused on improving, and making more realistic, some of the existing physical, chemical, and biological processes algorithms; 2). Adapting the methodology for use at larger spatial scales , or for use in concert with larger spatial scale modeling systems: and 3). adding provisions for applications to regulatory support problems.

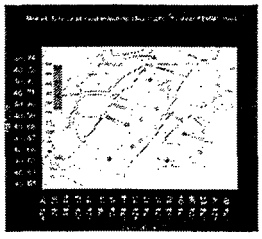
SOME RELEVANT SEDIMENT PROPERTIES

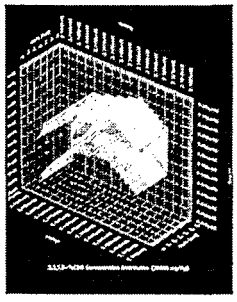
Contaminant distributions are heterogeneous in spatial distribution.

Sediments are very heterogeneous in size and composition.

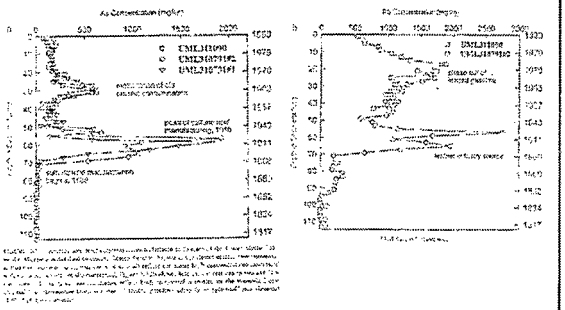


SPATIAL DISTRIBUTION OF CONTAMINANTS IN NY/NJ HARBOR SEDIMENTS

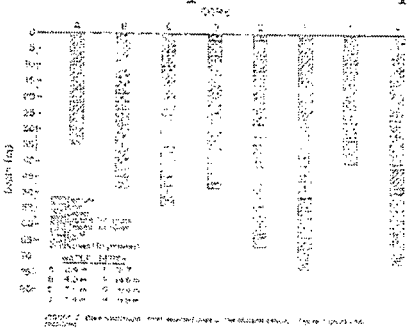




TYPICAL SURFACE SEDIMENTS FOUND IN THE PORT OF NY/NJ



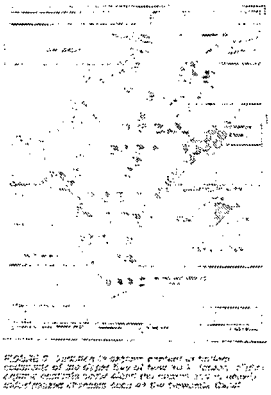
Sediment Composition vs. Depth



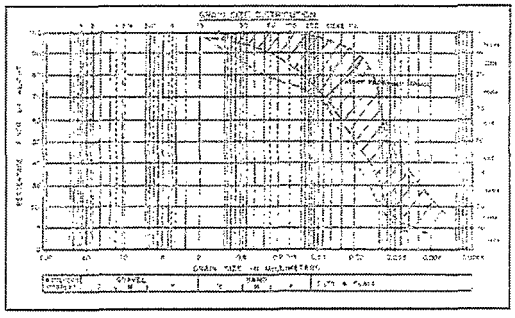
Sediment Characteristics

- Wide range of grain sizes
- A variety of analytical techniques are needed
- Extrapolation from grain size to larger scales is difficult

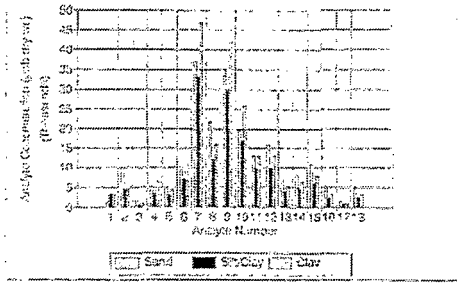
Carbon Content of Sediments



Sediment Size Distributions

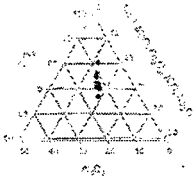


PAHs IN SAND, SILT/CLAY, AND CLAY



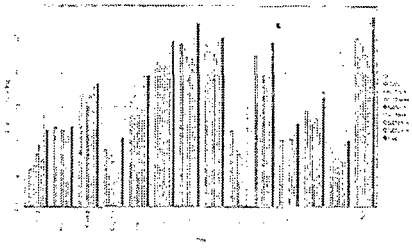
MAJOR OXIDE COMPOSITION FOR NY/NJ HARBOR SEDIMENTS: IMPORTANT FOR BENEFICIAL USE APPLICATIONS.

New York/New Jersey Harbor Dredged Material
Major Oxide Composition



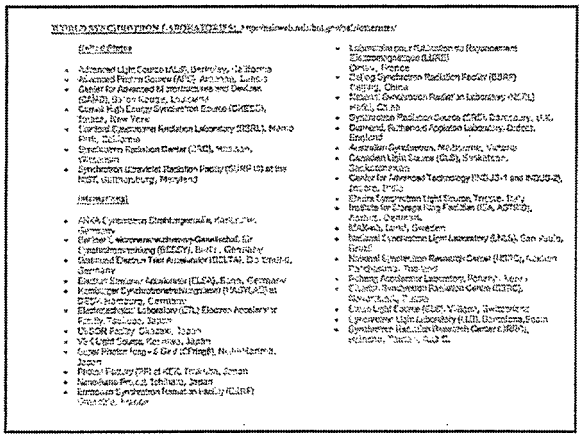
Marked region is optimum for cement production. Additives are used to adjust sediment composition to this region.

Metal Concentrations vs. Sediment Size Fraction

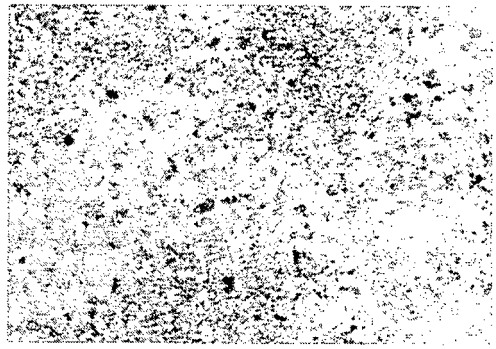


TYPES OF CONTAMINANTS

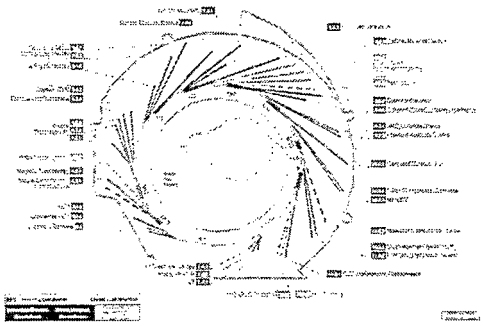
Contaminant	Sample Size	Analyte Size	Southern Central	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]			
[illegible]	[illegible]	[illegible]	[illegible]			
[illegible]	[illegible]	[illegible]	[illegible]			

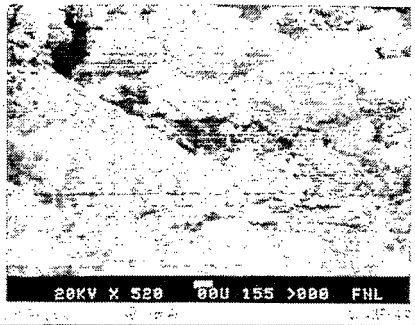


NIST SRM 1944. NY/NJ Harbor Sediments. 5.5 X



BEAM LINES AT THE LBNL ADVANCED LIGHT SOURCE

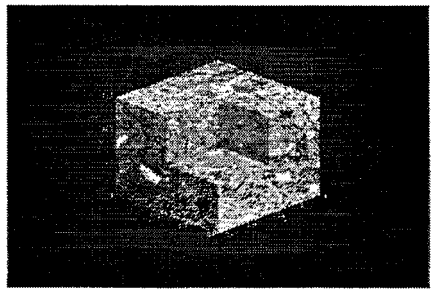




STEPS FOR DOING AN EXPERIMENT AT A SYNCHROTRON X-RAY FACILITY:

- Define the experiment, technique, and justification for use of a synchrotron x-ray source
- Select the synchrotron facility and the proper beam line
- Apply for time as a general user (can be in collaboration with beam line personnel). No cost for use of the facility.
- Beam time schedule following approval of proposal
- Travel to facility and perform experiment
- End-of-run evaluation
- Publish report/paper

Note that some facilities will pay for travel costs. Notably, the ESRF will support experimenters from EU countries.



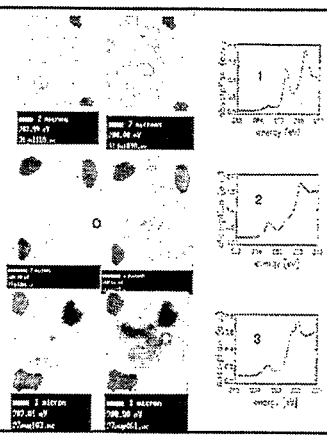
CMT volume of sandy sediments obtained from the New York/New Jersey Harbor.

X-RAY COMPUTED FLUORESCENT X-RAY TOMOGRAPHY: ESRF ID-11. With B. Vekemans, L. Vincze, I. Szaloki, F. Adams, R. Van Grieken, and C. Riekel.

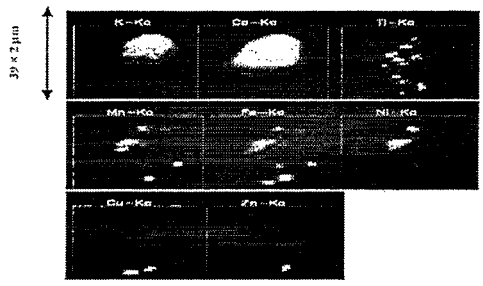
This experiment investigated the distribution of metals in single sediment particles. It showed that metals in some cases were present on the particle surface at isolated positions, but were not concentrated in a biofilm coating. Metals were also distributed in different ways through what is possibly an agglomerate of several particles.

X-RAY MICROSCOPY: NSLS X1A. With U. Neuhäusler, Stony Brook.

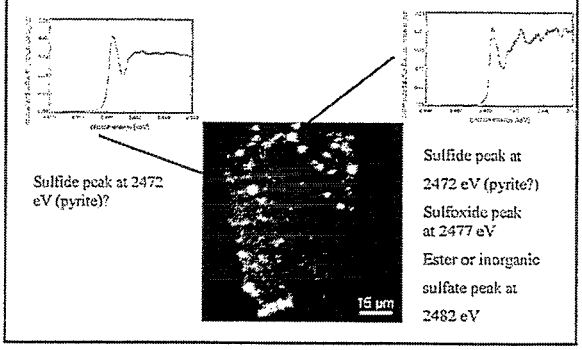
The top two rows of the figure show absorption maps of sediment particles after cleaning with the proprietary washing process of PinGeneris Enterprises. The bottom row shows results for the untreated sediments. XANES spectra obtained at the points marked are green are shown to the right of the maps. Spectra obtained for natural humin and fulvic acid materials are shown for comparison.



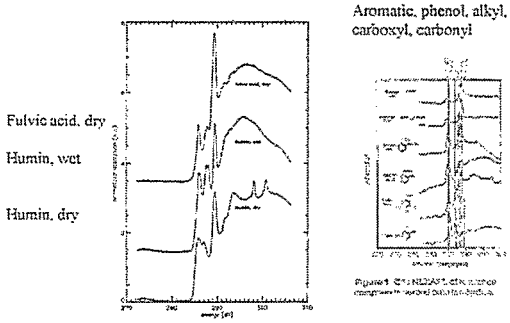
THE DISTRIBUTION OF K, CA, TI, MN, FE, NI, CU, AND ZN IN A 2 μm SECTION OF A SEDIMENT PARTICLE FROM THE NEW YORK/NEW JERSEY HARBOR.



S X-RAY MICROSCOPY AT THE ESRF ID 21 BEAM LINE

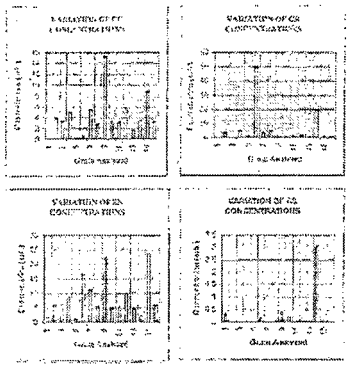


XANES SPECTRA FOR SEVERAL ORGANIC COMPOUNDS

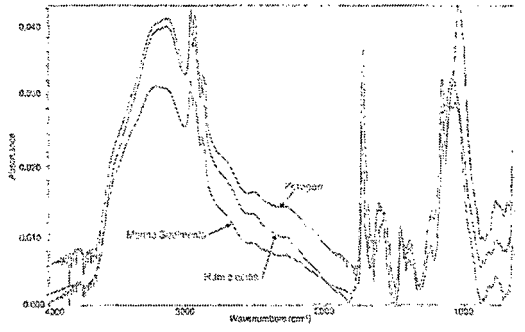


Neuhaeusler Ph.D thesis. Scheinhost et al. NSLS Abstract No. Sche7642.

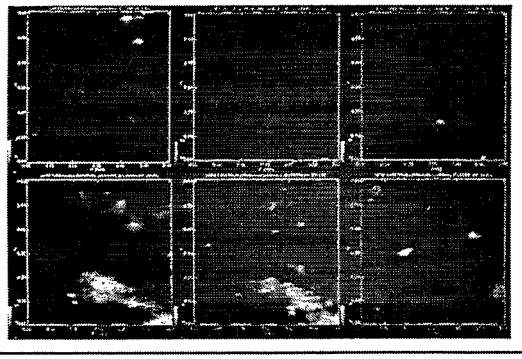
X-RAY FLUORESCENCE MICROPROBE: NSLS X26A BEAM LINE. With S. Song and A. Lanzirotti. Measurements were made on sediment grains with sizes greater than about .030 mm. Concentrations in the single points measured vary widely, but were observed in a majority of the particles investigated. Scans and maps were made on some of the particles in an effort to detect any surface enhancement resulting from partitioning of the metals to a surface biofilm, but no strong evidence was found to substantiate this possibility. We plan to investigate this further with smaller x-ray beams and improved sample preparation.



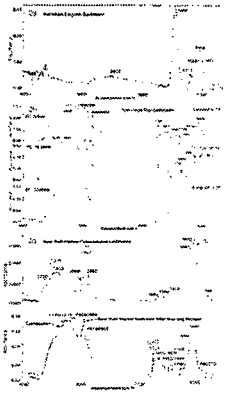
FTIR SPECTRA FOR HUMIC ACID, MARINE SEDIMENT, AND KEROGEN



NIST SRM 1944 – NY/NJ WATERWAY SEDIMENTS – S, NI, CU, ZN, PB. AND SR

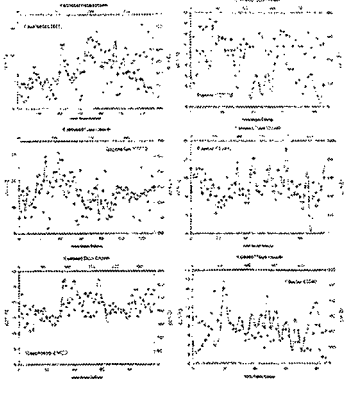


FTIR SPECTRA FOR SEDIMENTS FROM THE VENICE LAGOON, SAN DIEGO BAY, AND THE PORT OF NY/NJ

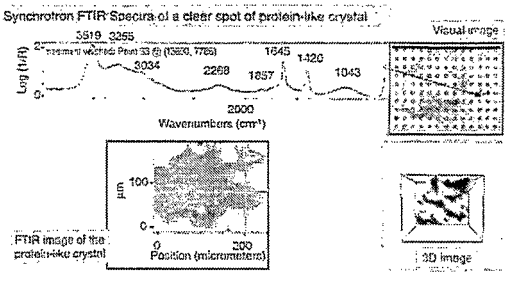


HUMAN HEALTH EFFECTS OF HG

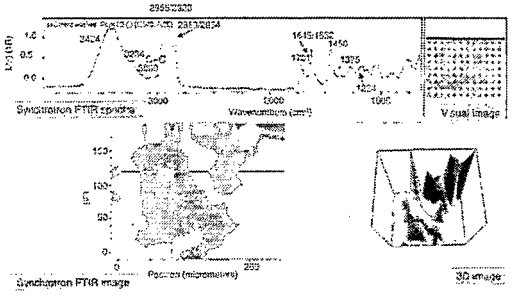
Studies on populations in the Faeroe and Seychelles Islands reached different conclusions. We used hair concentrations as an indicator for possible differences in Hg dose in the two studies



HIGH RESOLUTION FTIR-MAP OF EXTRACT FROM NY/NJ HARBOR SEDIMENT AFTER DECONTAMINATION USING A SEDIMENT WASHING TECHNOLOGY



HIGH RESOLUTION FTIR-MAP OF EXTRACT FROM NY/NJ HARBOR SEDIMENT AFTER DECONTAMINATION USING A SEDIMENT WASHING TECHNOLOGY



NATURAL ATTENUATION/BIOREMEDIATION INVESTIGATION

An initial look at natural attenuation/bioremediation in sediments from Newark Bay at South Kearny Point has been started. Bioremediation may have applications in sediments stored in confined disposal facilities or used in ecosystem restoration projects.

Meyers, R. E., and Williford, C. W. (2000). "Concepts and technologies for bioremediation in Confined Disposal Facilities," DOER Technical Notes Collection (ERDC TN-DOER-C11). U/S. Army Engineer Research and Development Center, Vicksburg, MS. www.wes.mil/el/dots/doer

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, but largely by aliphatic hydrocarbons and unknown nitrogen containing materials with a small portion of PAHs. Thus, contaminated sediments can be clearly identified and characterized by using FTIR techniques.

3. The effectiveness of sediment washing (BioGenesis Enterprises) technology for removing organic contaminants was shown. However, parts of the organic contaminants, namely aliphatic hydrocarbons, have been integrated through biogeochemical 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.

PURPOSE OF THE EXPERIMENT

The experimental objective is to evaluate the rate of natural attenuation for organic compounds under different conditions for electron donors and acceptors.

Emphasis is on the role of sulfate reducing bacteria (SRB) under anaerobic conditions. SRBs can destroy organic compounds and influence the speciation of heavy metals.

Samples include control, added sulfate (acceptor), added acetate (donor), and added sulfate and acetate.

Tests include most probable number test (MPN) to determine the number of endogenous bacteria, the BioMet test to assay bioavailability and biotoxicity, and synchrotron FTIR to investigate changes in functional groups.

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.

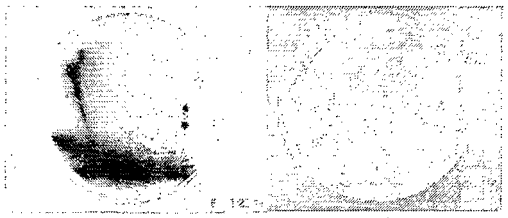
To clearly characterize the chemical properties and source of these organic contaminants the characterization of the water-soluble, organic-solvent-soluble, and the insoluble organic matter fractions in the sediments are necessary, as well as their distributions as a function of sediment particle size molecular weight.

The use of high-resolution synchrotron FTIR techniques is an essential tool for executing these investigations.

NATURAL ATTENUATION / REMEDIATION OF NY/NJ HARBOR SEDIMENT

- Aims of the project (ongoing):
  - Improve the quality of sediment by the activity of natural microbial populations or addition of polymers
    - Immobilization of heavy metals
    - Degradation / trapping of organics
  - Determine optimal storage conditions or alternative uses

MICROBIAL POPULATIONS IN SEDIMENT

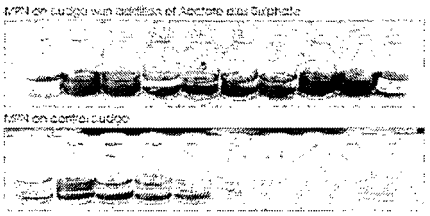


Sulfate reducing bacteria

Aerobic bacteria

USE OF BIOMET SENSORS TO ASSESS THE QUALITY OF SEDIMENTS AND BENEFICIAL USE PRODUCTS

EVALUATION OF THE SRB POPULATION



Strong decrease in redox potential accompanied by increase in the population of SRBs

EVALUATION OF PHYSICOCHEMICAL PARAMETERS – NATURAL ATTENUATION

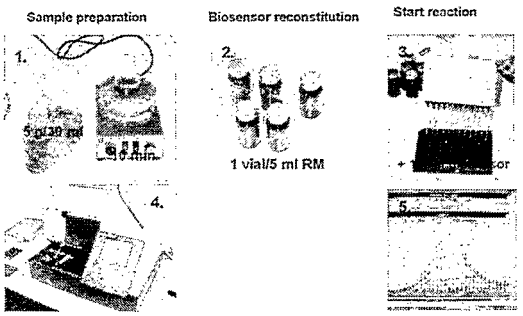
Sample	Zn	[illegible]
Control	[illegible]	[illegible]
+ Acetate	n.d.	[illegible]
+ Sulfate	n.d.	[illegible]
+ Acetate + Sulfate	n.d.	[illegible]
[illegible]	[illegible]	[illegible]

After 7 weeks a strong reduction in Zn bioavailability is observed for all conditions tested, due to anaerobic conditions

Sample	Eh	[illegible]
Control	[illegible]	[illegible]
+ Acetate		[illegible]
+ Sulfate		[illegible]
+ Acetate + Sulfate		[illegible]

Strongest decrease in redox potential observed when both electron donor plus acceptor are added

BASIC BIOMET® PROTOCOL



EVALUATION PARAMETERS – PHYSICOCHEMICAL TREATMENT

Sample	Total Zinc	Bioavailable Zinc	Toxicity value
Contaminated harbor sludge	455	175	0.4
Soil washed harbor sludge	n.d.	n.d.	0.4
Polymer treated harbor sludge	n.d.	162	0.9

Total zinc in ppm
Bioavailable zinc in ppm per kg dry weight sludge
Toxicity value: percentage lysis compared to non-toxic control

- Soil washing removed heavy metals but did not reduce toxicity
- Polymers addition did not result in a decreased heavy zinc bioavailability, but bound toxic organic compounds

EDUCATIONAL AND OUTREACH PROGRAMS

The results of sediment science must be disseminated to several audiences if they are to be useful:

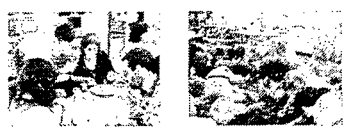
Scientific, engineering, and regulatory communities for incorporation in remediation projects, risk assessment, planning work, etc.

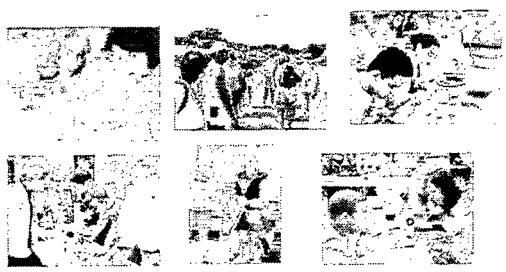
Science education at all levels

Community outreach/education for gaining support for environmental projects.

COMMUNITY OUTREACH MEETING IN BROOKLYN, NY

NY/NJ Harbor Sediment Decontamination Demonstration Community Outreach Program sponsored participation by elementary school teachers from Kearny, NJ at the Rutgers Marine Activities, Resources, and Education Summer Institute, August 5-10, 2001.



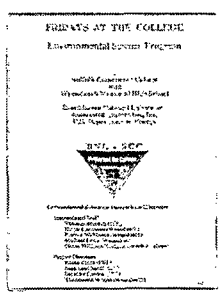


SUMMARY AND CONCLUSIONS

Investigations of sediment properties is aided by measurements on the molecular- and grain-size scales.

The results can be used to improve models for the fate and transport of contaminants at larger size scales.

Similar experiments can be conducted on Latvian sediments.

Sediment problems exist around the world. Cooperative experiments can be carried out with other institutions in Europe and elsewhere.

ENVIRONMENTAL EDUCATION AT HIGH SCHOOL AND JUNIOR COLLEGE LEVELS