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Coping with Contaminated Sediments and Soils in the Urban Environment

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COPING WITH CONTAMINATED SEDIMENTS AND SOILS IN THE URBAN ENVIRONMENT

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ABSTRACT

Soils and sediments contaminated with toxic organic and inorganic compounds harmful to the environment and to human health are common in the urban environment. We report here on aspects of a program being carried out in the New York/New Jersey Port region to develop methods for processing dredged material from the Port to make products that are safe for introduction to commercial markets. We discuss some of the results of the program in Computational Environmental Science, Laboratory Environmental Science, and Applied Environmental Science and indicate some possible directions for future work. Overall, the program elements integrate the scientific and engineering aspects with regulatory, commercial, urban planning, local governments, and community group interests. Well-developed connections between these components are

critical to the ultimate success of efforts to cope with the problems caused by contaminated urban soils and sediments.

KEYWORDS

NY/NJ Harbor, sediments, decontamination, beneficial use, sediment characterization, environmental computing

INTRODUCTION

The functioning of mega-scale urban conglomerates is dependent on the interaction of numerous entities that provide government, food, electricity, transportation and all the other goods and services needed by its human population. But, as Empedocles proposed almost 2500 years ago, the world is composed of the four elements of fire, water, air, and earth. Today, we may consider that these elements are the foundations for our urban cultures with fire equated to energy sources and air, water, and earth being the veritable bases of our lives. Unfortunately, human activities can cause contamination of our surroundings with toxic organic and inorganic compounds that harm the environment and human health. The pathways for the compounds in the environment are complex and involve multi-directional interactions between the air, water, and earth on both a micro and macro scale. While working to ensure that urban regions have clean air, water, and earth, we need to also pay attention to processes occurring on regional or global scales.

The New York/New Jersey Harbor region shown in Figure 1 is a good illustrative example of the transport and fate of contaminants in an urban system. Anthropogenic contaminants have entered and continue to enter the system through a variety of pathways including both point and non-point sources in the 35,000 square kilometer watershed. Historically, poor waste management practices resulted in releases of these materials. These contaminants, particularly lipophilic non-polar compounds and organometals like mercury, became bound to the organically rich sediments of the harbor. Over time, these sediments have been transported via the highly dynamic estuarine hydrology to various locations resulting in "toxic hot spots". These sediments, rather than being removed from the system through burial, are continually disturbed by normal tidal action, storm water scour, and dredging activities making the associated chemicals available for exposure to benthic communities, and thereby entering the estuarine food chain and eventually the human food supply.

There is also a direct practical aspect resulting from the sediment contamination. Maintenance of efficient operation of the Port of New York/New Jersey requires dredging of the navigational channels in the Port on a regular basis. The amounts vary from year-to-year, but average around 1,000,000 to 1,500,000 m^3 /year. Consequently, better than half the material is considered too contaminated for unrestricted ocean disposal due to either toxicity or bioaccumulation potential. Stringent regulations govern the ways in which this material can be managed. Since Port operations are vital to the economic viability of the NY/NJ urban region, over the past decade, the region has invested considerable resources to develop creative, yet environmentally responsible, ways for managing this material. This is being done through an innovative cooperative inter-agency process to pursue a policy of reduction in dredging, reduction in pollution, beneficial use, and minimization of disposal. Douglas et al. (2004) have given a review of the status of contaminated dredged material management in the Port region.

We summarize here work relevant to the development of methods that can be used to economically process/ decontaminate sediments and soils to create environmentally acceptable beneficial use products. The decontamination technology is part of an overall treatment train that includes dredging, transport to a processing site, decontamination, creation of a beneficial use product, and shipment to the site of the end use. Fees paid by the beneficiaries of the dredging or remediation operation and the sale of beneficial use products pay for the treatment train operation.

Technologies investigated included solidification/stabilization, manufactured soil creation from untreated sediments, sediment/soil washing, solvent extraction, thermal desorption, and very high temperature treatments. They are applicable to sediments or soils that are lightly (washing) or heavily (thermal) contaminated and combined are the basis for a treatment train that can be used to effectively manage the contaminated sediments and soils found in urban regions.

The practical demonstrations have been supported by other activities. They include a computational capability that uses open source software to provide interactive modeling and visualization resources for interested users. Additionally, research and development efforts are carried out to improve our understanding of the biological, chemical, and physical interactions that govern the interactions of the contaminants with the sediments. This effort is integrated with the large-scale demonstrations and with the computational modeling work.

Our project approach to contaminated soils/sediments in New York and New Jersey is also generally applicable to urban sites around the world with similar problems.

Specifically, it could well be of benefit to projects in Shanghai and other regions of China.

COMPUTATIONAL ENVIRONMENTAL SCIENCE

Handling the variety of data related to management of contaminated sediments and soils is a challenging problem for computational science because of the size and complexity of data sets, the broad range of interests and needs of the regulatory agencies, governmental agencies, community and environmental groups, commercial contractors, research groups, and educational institutions. Fortunately, the tools that are needed to respond to these needs are rapidly becoming available through recent advances in computer science. The challenge is to produce an integrated system that deals with an integrated database and gives an easily understandable user interface with tools for viewing and manipulating selected portions of the overall library. There is a need for integration of existing resources so that individuals from all the above groups can work with the data and obtain answers to their questions. In doing this, it is important to reduce the need to down load and install programs on individual computers or to require the user to work with proprietary soft ware.

Initial work on the outlined concept is underway. **A** web interface for distributed collaboration is being assembled. It will use a variety of computer systems for doing large-scale calculations using parallel computing and distributed computing based on grid concepts to provide sufficient hardware resources. For some problems, specialized computers such as graphics clusters for large-scale visualization and simulation or a machine such as QCDOC, a Columbia-BNL machine originally designed for high-energy physics calculations that is capable of computing 10 Trillion floating-point operations per second, will be used.

The Web interface for distributed collaboration will interface to: Open geographic information system (GIS) mapping tool (GRASS, http://www.grass.org/); visualization tools (GIMP, http://www.gimp.org (OpendDX, http://www.opendx.org/) and specialized software for dealing with scientific data and large data bases of environmental results; and fluid flow simulations (Lattice Boltzmann Model, http://math.nist.gov/mcsd/savg/vis/fluid/index.html, and others to cover flow fi-om the micro scale to watershed scale); and Grid tools to facilitate remote use and access to distributed data bases. The interface is being built using Java and client server architectures, and authorization protocols.

Grid computing will **raise** the development of global environmental collaborations and sharing of resources to a new level where interactive work can be done between different regions that face common problems. Grid computing can couple applications to high-speed network infrastructures and manage distributed users, data, and computing resources on a global scale. High performance networking requires attention to high- speed monitoring, authentication, and security issues. Environmental models often involve large-scale computations that benefit fi-om use of parallel computations that distribute applications and data across multiple grid-based computers. Visualization of the results is enhanced through interactive exploration and visualization of the data

Data taken from an extensive investigation of the contaminants in the Passaic River in New Jersey serves as a good example of the way that visualization can help planners concerned with the environmental health of the river. Over 100 core samples were taken over a 15 km stretch of the river and analyzed for both organic and inorganic contaminants (R-EMAP, 1998). The results were presented using the OpenDX visualization software and a specialized interpolation formalism by Ma et al. (1998). The three-dimensional distribution of 2,3,7,8 TCDD released from long-term industrial waste disposal processes that resulted in direct or indirect discharge of waste, sludge, and dioxin product into the river is shown in Figure 2. The view is striking since the sediments are still well localized showing that the sediments were ultimately very effectively buried at the original site although there was initially a wide dispersion of dioxin around the Harbor. Analysis of the visualized data can give an estimate of the volume of the contaminated material at this "hot spot" and serve as the basis for considering decisions on possible removal work. Very recently, Feng et al. (2004) considered a more extensive data set in terms of a GIS format.

We have also used the Lattice Boltzmann model to follow the flow of a fluid through an experimentally determined microstructure of sediments from the New York/New Jersey Harbor. The results of the calculation are shown in Figure 3. The lightest blue represents pore space and the darker values show individual grains. The colored regions indicate the pore space filled with liquid being injected into the sediment. The percolation of the fluid can thus be followed through the sediments to show how a contaminant will diffuse through the material.

EXPERIMENTAL ENVIRONMENTAL SCIENCE

Understanding the transport and fate of toxic materials in soils and sediments requires knowledge of their properties on scales from the molecular to the regional. **A** variety of analytical tools are needed for the characterization. Many of these tools are widely used and are widely available in environmental laboratories. Examples of the techniques include mass spectroscopy, gas and liquid chromatography, and electron microscopy. There is clearly room for use of other experimental techniques that are not so commonplace or that advance the state-of-the-art in environmental science investigations. In this section we present several examples that are relevant to the problems associated with contaminated sediments in the NY/NJ region.

Experiments Using the Synchrotron X-ray Source:

Synchrotron radiation x-ray sources are recognized as a major tool for environmental investigations. The synchrotron source is based on the application of accelerator technology to produce intense beams of high-energy electrons or positrons that are guided into closed orbits using magnetic fields. As they circulate, the particles radiate electromagnetic radiation with energies that range from the far infi-ared to high-energy x radiation. The intensity of the radiation is far higher than the intensity produced by laboratory sources and this makes possible experiments of much greater sophistication. Synchrotron sources are expensive and large-scale facilities with construction costs in the range of hundreds of millions of US dollars and are operated with large technical staffs. Nevertheless, there are some 40 facilities in operation or being constructed around the world with users numbering in thousands. The state of synchrotron-based science has been reviewed in several recent books (van Grieken et al., 1992, Sham, T. S. et al. 2002, Fenter, P. et al., 2002).

Our group has been fortunate in having convenient access to a leading synchrotron facility located at Brookhaven National Laboratory, the National Synchrotron Light Source (NSLS). Information on the NSLS can be found at the web site: http://www.nsls.bnl.,gov/. The characteristics of several facilities are shown in Figure 4 in comparison with those for laboratory instruments. Here it is evident that the synchrotron source is around 10,000 times higher in intensity than a laboratoty source thus showing the attractiveness for research applications. We mention below several experiments that are relevant to contaminated sediments in NY/NJ Harbor.

?? Micrometer-scale mapping of organic compounds using Fourier Transform Infrared Spectroscopy (FTIR). We measured FTIR spectra for several different types of sediments and of humic and fulvic acid samples. Comparing the results showed that compounds with a strong C-H stretch bonding typical of compounds such as polynuclear aromatic hydrocarbons in the vicinity of the 2800 cm^{-1} region occurred in contaminated sediments, but not in the other materials. This indicates that it is plausible to identify such compounds as arising from anthropogenic activities. FTIR spectroscopy may therefore be a rapid screening tool for identifying contaminated sediments that could require decontamination. Of course, at this point, the approach is not specific to particular organic compounds and thus is a qualitative indicator only.

?? Morphology of individual sediment particles and the interaction of organic compounds with sediment particles of sand and clays can be examined using x-ray microscopy. We measured the x-ray transmission of selected regions in the sediment sample to get information on their shapes and composition. A scan of a particle surrounded by a cloud of organic compounds is shown in Figure 5. The darker region is an inorganic sediment particle and the lighter region is a carbonaceous organic particle. Measurement of the absorption as a function of the x-ray energy gives information on the chemical form of the organics compounds. This is similar to the type of results found using the IR techmque. Ultimately, it will be possible to discern how the organic materials are distributed in the sediments and to gain a better understanding of their interaction with the inorganic sediment particles.

?? The morphology of ensembles of sediment particles can be measured with the technique of synchrotroil-computed microtomography (CMT). This is similar to concept to a medical CAT scan although producing a true 3-dimensional image of the structure of the sediments and the included pore space. The measurements can be based on the amount of absorption of the x rays or on the emission of characteristic elements such as lead. The results are used as the basis for understanding how fluids follow through the materials and for how the contaminants react with the surfaces of the sediments. Understanding of transport and fate of the contaminants on the grain-size scale leads to better modeling of transport on a harbor-wide scale and can thus be an asset in making decisions on the environmental impact of the contaminants. We displayed an example of the transport and modeling in the discussion of computational aspects of environmental science presented above (See Figure 3).

?? X-ray microprobe measurements based on detection of characteristic elemental x rays can make 2- or 3-dimensional maps of elemental distributions with detection limits below 10^{-15} g spatial resolutions of micrometers. One way that we have employed this technique is to measure the spatial distribution of mercury along the length of individual human hairs. The hair concentration gives an indication of the mercury concentration in the body as a function of time. We compared the concentrations in hair samples taken from fish-eating populations in the Seychelles and Faeroe Islands. Results of these studies have been used as a basis for setting levels for human exposure in the United States. However, there were disagreements on the conclusions drawn from the studies. The results we obtained showed that the exposures for the two groups were similar and that short-term peak exposures could not help to explain the differences in the study conclusions. We also used this technique to measure the spatial distribution and chemical oxidation state of contaminant metals on sediments from several locations. Since mercury is found in the harbor and can contribute to mercury uptake in our location through fish consumption, the hair measurements have relevance to the problem of the ultimate fate of mercury found in the harbor.

Laser-based Mercury Detection:

Real-time detection of mercury in the atmosphere is useful for investigating sources of mercury and gives the basis for understanding the amount of mercury entering sediments in the Harbor from atmospheric deposition. Conventional methods require sampling over extended periods of time in order to reach acceptable levels of detection sensitivity. Development of new methods for measuring mercury is needed so that results can be obtained to help in understanding wind direction dependence and for understanding variations in output from coal burning power plants arising from changes in the type of coal being burned.

Proof-of-principle experiments on the real-time detection of ppt levels of Hg using the cavity ringdown technique were conducted. Cavity ringdown spectroscopy has been able to achieve this level of sensitivity because this approach measures the *rate of absorption* rather than directly monitoring the change in the probe light intensity. By measuring the rate of absorption, the CRD measurement process becomes independent of light source intensity fluctuations thereby increasing attainable detection sensitivities. In CRD, a monochromatic light pulse is injected into a high Q-value optical cavity. A detector is positioned at the exit end of the cavity to monitor the light leakage of the injected light pulse per round trip. Using very highly reflective mirrors, the injected laser pulse will male several thousand round trips between the two cavity mirrors. Each round trip will result in a slight loss of intensity due to transmission loses at each mirror and other finite losses in the system. This loss will follow a simple exponential decay. When an absorbing sample is then placed in the cavity, the loss per round trip will exceed that of the empty cavity thereby resulting in a different decay. When this measurement is conducted as a function of wavelength a high-sensitivity absorption spectra can be reconstructed for a given chemical species. The time necessary for the intensity (amplitude) of the injected light pulse to decay to 1/e of its initial value is referred to as the "ringdown" time, and from which this spectroscopy derives its name. Typically, the decay time to the 1/e value is on the order of tens of microseconds, but is very dependent upon the reflectivity of the mirrors. Consequently, a CRD signal is collected for each laser pulse and subsequently averaged until the desired signal-to-noise ratio (SNR) is achieved.

The system was tested by collecting air samples in New Jersey at several points in the Harbor and then bringing them to Brookhaven for analysis. The results obtained were similar to previously measured values obtained using conventional methods by a group at Stevens Institute of Technology and Rutgers University (Korfiatis et. al., 2003). The instrument can be made mobile for long-term operation at remote locations for extended monitoring operations.

Microbial Applications:

Microbes are of great importance in the world we live in and are certainly important in sediments and soils. In dealing with contamination, they can be a means of natural attenuation by using organic compounds, including contaminants, as a carbon source and/or electron donor, and as part of their respiratoiy process change via direct or indirect reduction the oxidation state of metals to a relatively insoluble form. They can also be used as indicators for bioaccumulation and biotoxicity of a wide range of contaminants in the environment. Initial work on microbial activities found in sediments from NY/NJ Harbor show that endogenous sulfate reducing bacteria exist in sufficient quantities to be a potentially useful approach to producing insoluble metal sulfides in anoxic regions of sediments. Combining the usefulness of sulfate reducing bacteria in destruction of the organic compounds, including PAH, and immobilizing the metals under the form of metal sulfides (Rothermich et al., 2002) implies that natural attenuation could be an important strategy for solving the problem of contaminated sediment handling. Metal specific microbial biosensors, based on engineered heavy metal resistant bacteria that produce a detectable signal when sensing specific heavy metals in their environment, can be used as indicators of biotoxicity and bioavailability of particular metals, such as zinc, cadmium, lead and mercury (van der Lelie et al., 1999; Corbisier et al., 2000). The method was successfully employed to test properties of untreated and treated sediments fi-om NY/NJ Harbor.

APPLIED ENVIRONMENTAL SCIENCE: ENGINEERING DEMONSTRATIONS

The ultimate objective of our work is to develop sediment/soil decontamination technologies that can be used as one of the tools required for management of contaminated sediments in the NY/NJ region. The yearly need for upland disposal of sediments is of the order of 1,500,000 m^3. There is a range of contaminant levels found in this material so that different types of decontamination methods can have niche usefulness. High-temperature technologies are very effective and produce excellent beneficial use products, but generally are capital intensive and have increased operating expenses because of fuel costs. Low temperature methods are found to be less effective in dealing with contamination, but can have wide use in processing less heavily contaminated materials.

Over the past 10 years, the U. S. Environmental Protection Agency, New Jersey Department of Transportation, and Brookhaven National Laboratory solicited input from a large number of technology providers. Sequential tests of many techniques have been carried out on a scales ranging from 20 1 to several m^3 and finally, in the near future, to levels up to or above 15,000 m^3. (http://www.bnl.gov/wrdadcon, http://www.state.ni.us/transportation/works/maritime/>As a result of the testing work, two large-scale tests are being carried out that involve EPA, NJDOT, **BNL,** the technology groups, and site owners. One large-scale test using a high-temperature rotaiy kiln is being performed by Endesco Clean Harbors (ECH) in Bayonne, NJ. ECH is a subsidiary of the Gas Technology Institute (Des Plaines, IL). The other test is a sediment-washing technology of BioGenesis Enterprises to be carried out at Keasbey, NJ. Completion of the large-scale tests will be a major accomplishment in installing decontamination as a recognized component of an overall dredged material management plan whether for the Port of NY/NJ or for other regions. Both of these technologies are described below.

A simplified diagram of the Cement-Lock process is given in Figure 6. The sediment is blended with mineral modifiers and passed through a rotary kiln melter operating at about 1371 degrees C. The temperature is sufficient to destroy organic compounds and to completely melt the sediment and mineral modifiers. The molten material flows from the kiln and is quickly cooled. The resultant material – Ecomelt® – is ground to a powder and used to produce cement that can be sold and used in construction projects. The kiln being used for the Cement-Lock demonstration project is relatively small compared to kilns used for production of lightweight aggregate or for commercial Portland cement production. It has a length of 9.14 m with a diameter of 3.16 m compared to a typical cement kiln size of around 45 to 180 m in length **x** 4 m diameter that is operated at a temperature of 1480 degrees C. **A** photograph of the Cement-Lock demonstration plant installed in Bayonne, NJ is given in Figure 7. The yearly capacity of this system is 7,650 m^3 per year so that it serves mainly as a proof-of-principal facility.

The BioGenesis system uses high-pressure water jets to break up agglomerates of particles and to strip organic coating from the sediment particles. Surfactants are added to break bonds between the organic components and the sands and clays of the sediments or soils and chelators are added to convert metals into a soluble form that can then be extracted during the course of treating the process water. A process flow diagram is given in Figure 8 and a photograph of the equipment used for a pilot-scale demonstration carried out in Kearny, NJ in 1999 is shown in Figure 9. The cleaned sediment can be used to produce a manufactured soil suitable for sale as a residential soil. The designed throughput for the large-scale plant is about 180,000 m^3 /year.

Completion of the large-scale tests will be a major accomplishment in installing decontamination as a recognized component for an overall dredged material management plan whether for the Port of NY/NJ or for other regions.

SUMMARY

We believe that the combination of computational resources, synchrotron microbeam techniques that focus on micro-scale analysis, and general analytical instruments such as inductively-coupled mass spectrometiy and gas-chromatography mass spectrometry for bulk sample analysis is a powerful combination for environmental research and development. Information can be obtained that is beyond the reach of laboratory analytical instrumentation alone. This is particularly important for characterizing the physically and chemically complex NY/NJ Harbor system.

In summary, then, an even broader program is required for understanding not only the transport and fate of contaminants in sediments and soils, but also for developing environmentally sound and economically feasible methods for removing toxic compounds fi-om the sediments then turning them into useful products. The components for a program of this type include:

?? Use of interactive computing facilities for dissemination and analysis of data to a variety of stakeholders.

?? A close coupling betweeu scientific investigations and their application to field-scale remediation tasks is needed to ensure the quality of the decontamination and beneficial use technologies employed.

?? Close cooperation between the coinmercial entities that run the treatment plants, the providers of sediment, and the providers of capital and operating funds is necessary for long term success of the operation of decontamination facilities on a commercial scale.

Our work in the NY/NJ region described here is an example of this type of approach to dealing with contaminated sediments and soils.

ACKNOWLEDGMENTS

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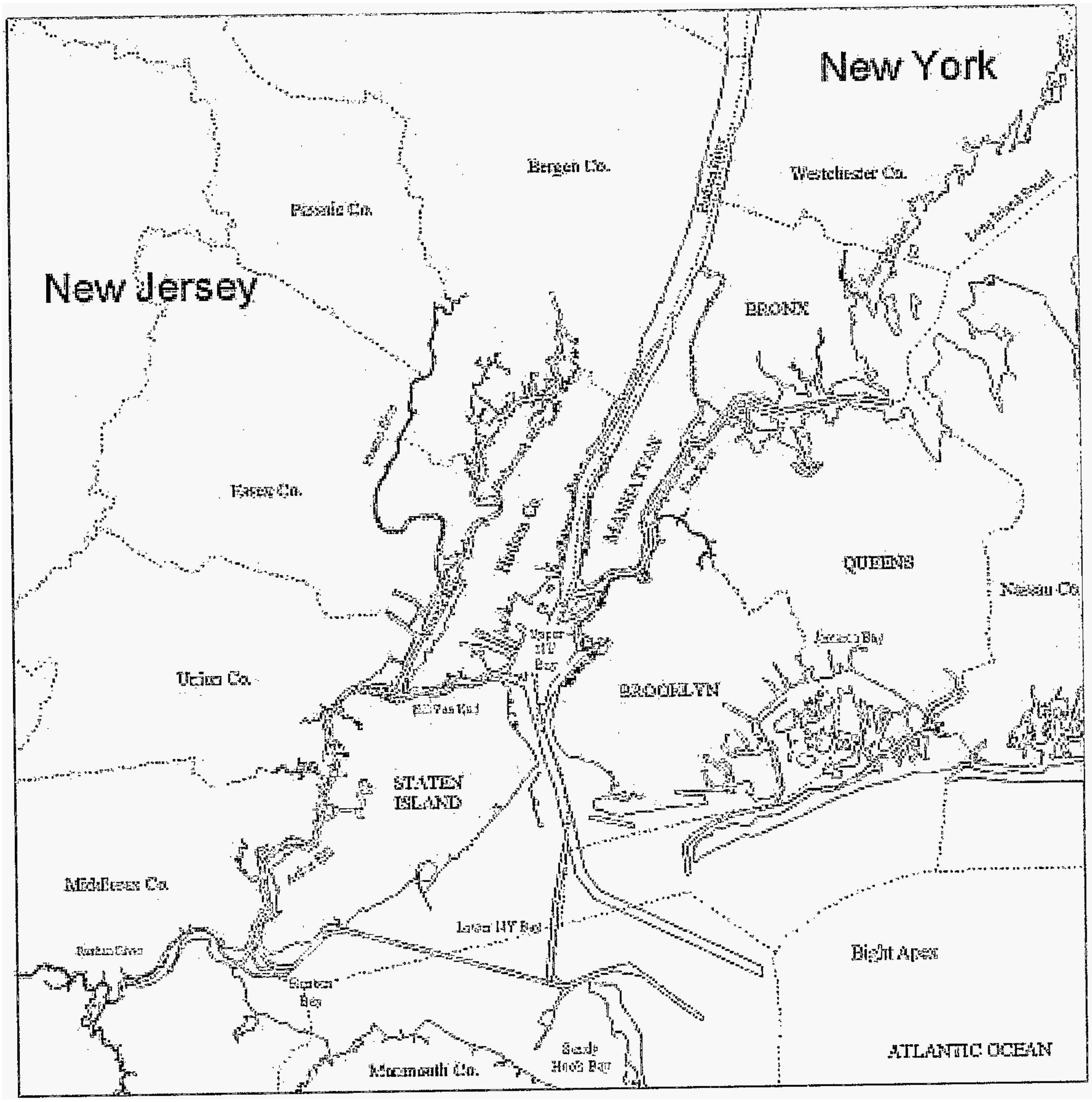

Figure 1. A map of the New York/New Jersey waterways that are central to the problems of contaminated sediments and soils considered here. Maintenance of the navigational channels of the Port of New York/New Jersey requires removal of around 1,000,000 m^3 each year.

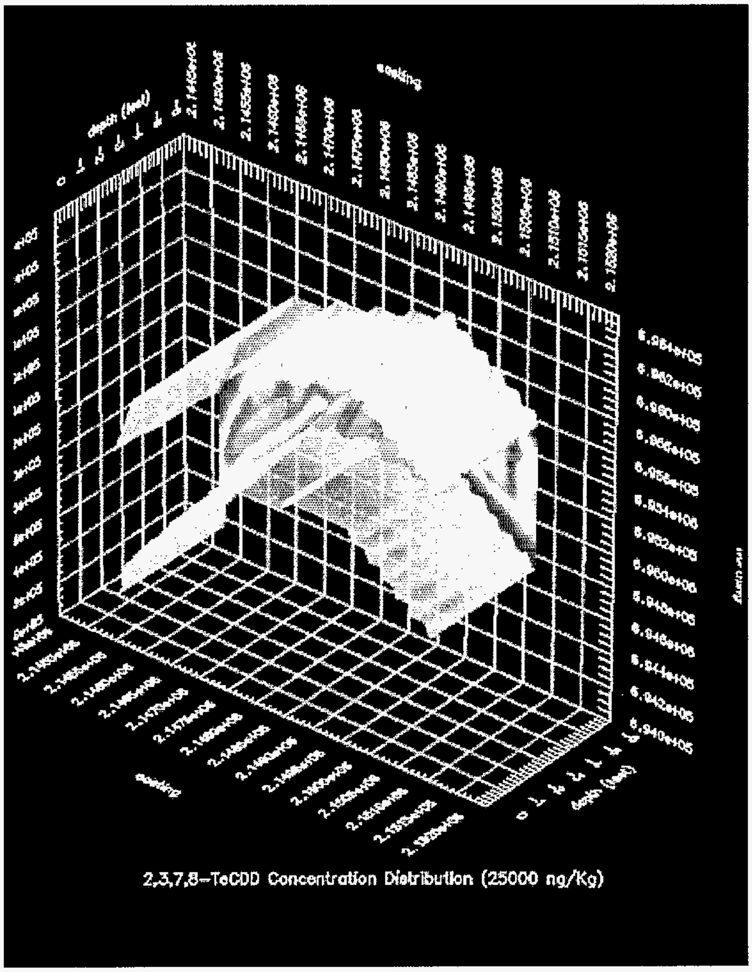

Figure 2. A three-dimensional view of concentrations of 2,3,7,8 TCDD in the Passaic River in New Jersey is given to illustrate the need for graphical visualization of contaminant distributions as the basis for management decisions.

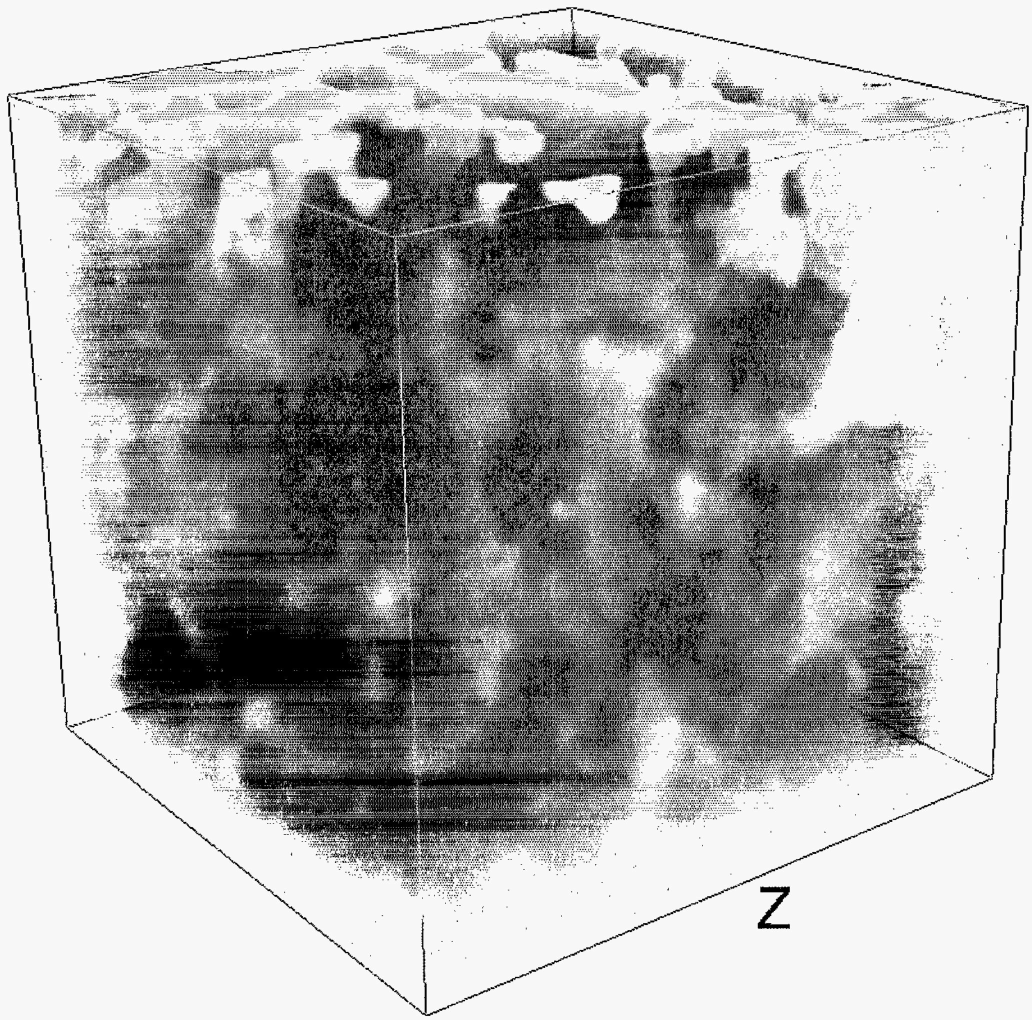

Figure 3. Experimental data obtained at the Brookhaven National Synchrotron Light Source was used to study fluid flow through ***NY*** Harbor sediment at the grain-scale level. The figure displays a portion of the data in a lattice 64 x 64 x64 pixels. The pixel size is 0.0067 mm. The pore space is shone in white and the solids in blue. The red and yellow represents flow of a contaminant calculated with a micro-scale fluid flow model. Incorporation of an interaction between the fluid and the solid material will ultimately increase our understanding of how the contaminants will accumulate on different mineral surfaces.

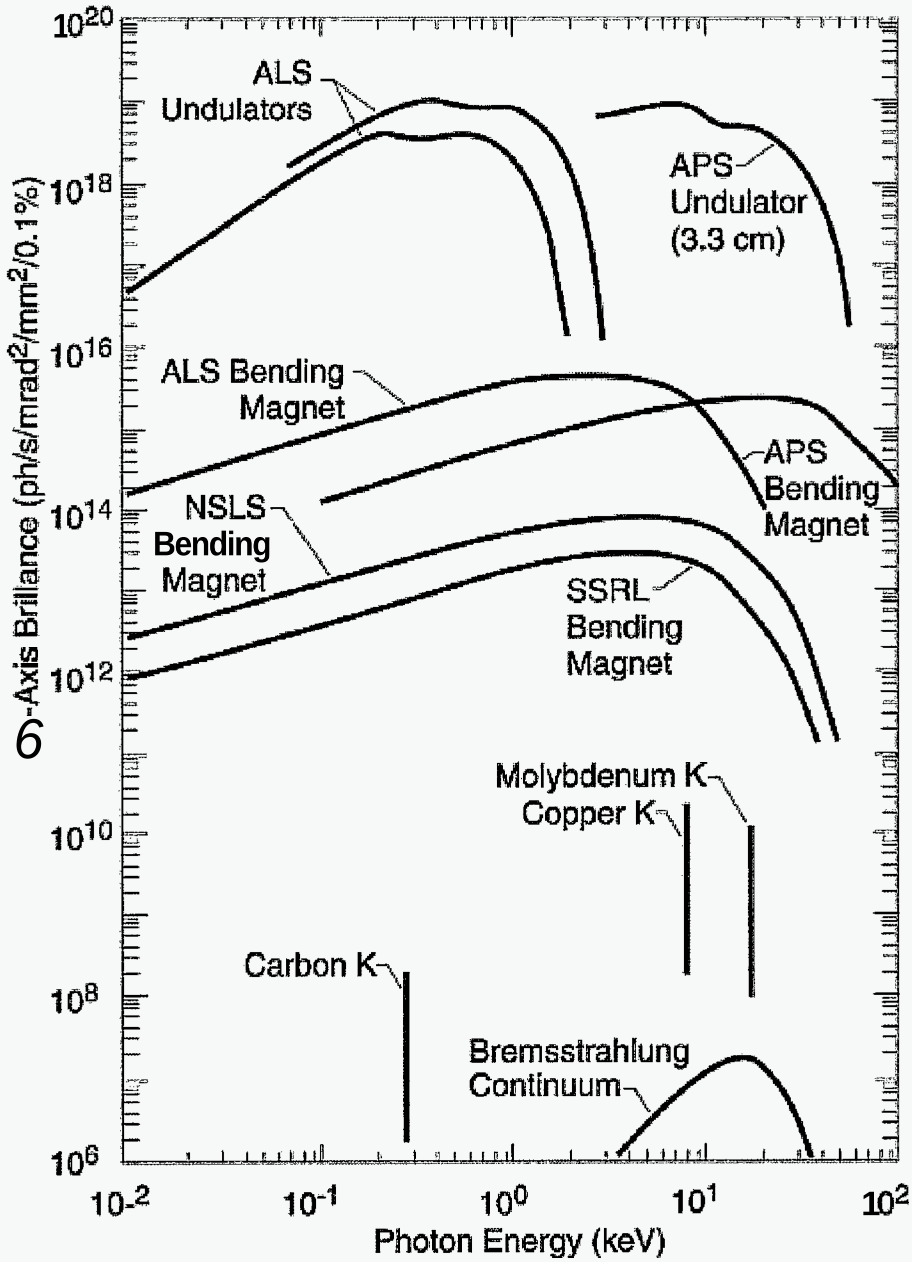

Figure 4. Brilliance is one of the key parameters that shows how intense the x-ray beam will be after it is focused into a small spot. This figure shows the values obtained at different facilities and using conventional x-ray tubes. The superiority of the synchrotron source for production of micro beams is clearly illustrated.

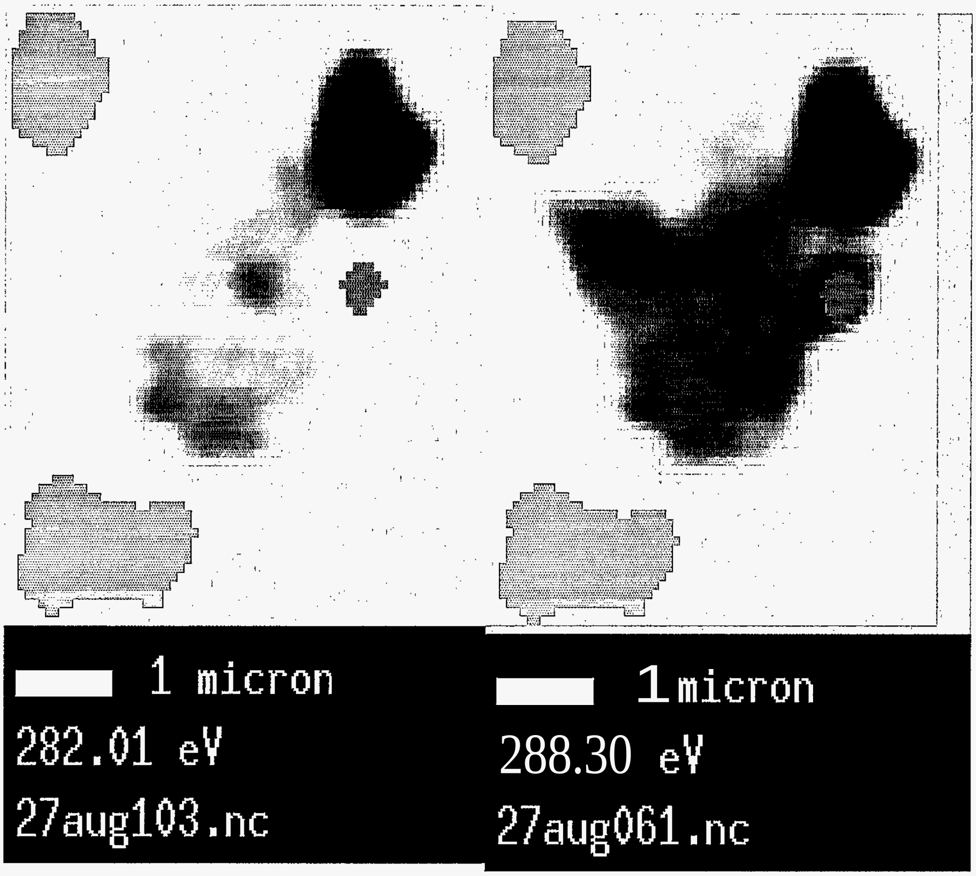

Figure 5. X-ray radiographs of a small particle of sediment fi-om the New York/ New Jersey Harbor taken with the x-ray microscope at the Brookhaven National Synchrotron Light Source. The panel at the left is taken below the carbon K-x ray absorption edge. The panel at the right was taken above the K-absorption edge. Carbon is identified by an increase in the absorption signaled by a blacker image in the right-hand panel. Sediment particles do not show such a dramatic change. The red and green spots show regions used for normalization of the scans and spots where determinations were made of the carbon compounds functional groups using x-ray near edge absorption spectroscopy.

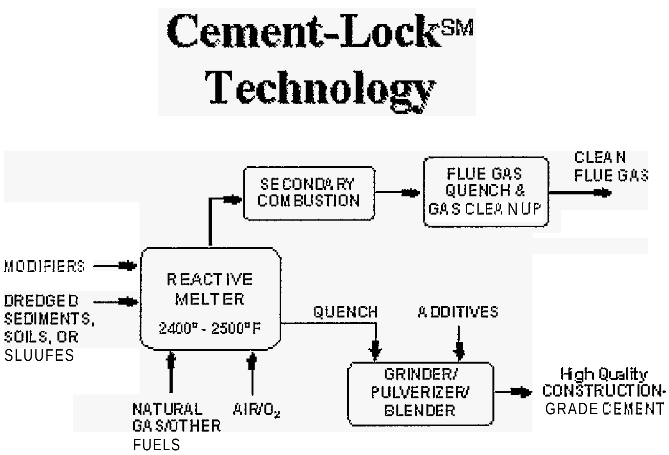

Figure 6. The process flow diagram for the high-temperature rotary kiln process of Endesco is shown here in a simplified form. Modifiers are added to produce a product that is appropriate for the ultimate beneficial use as a component of cement.

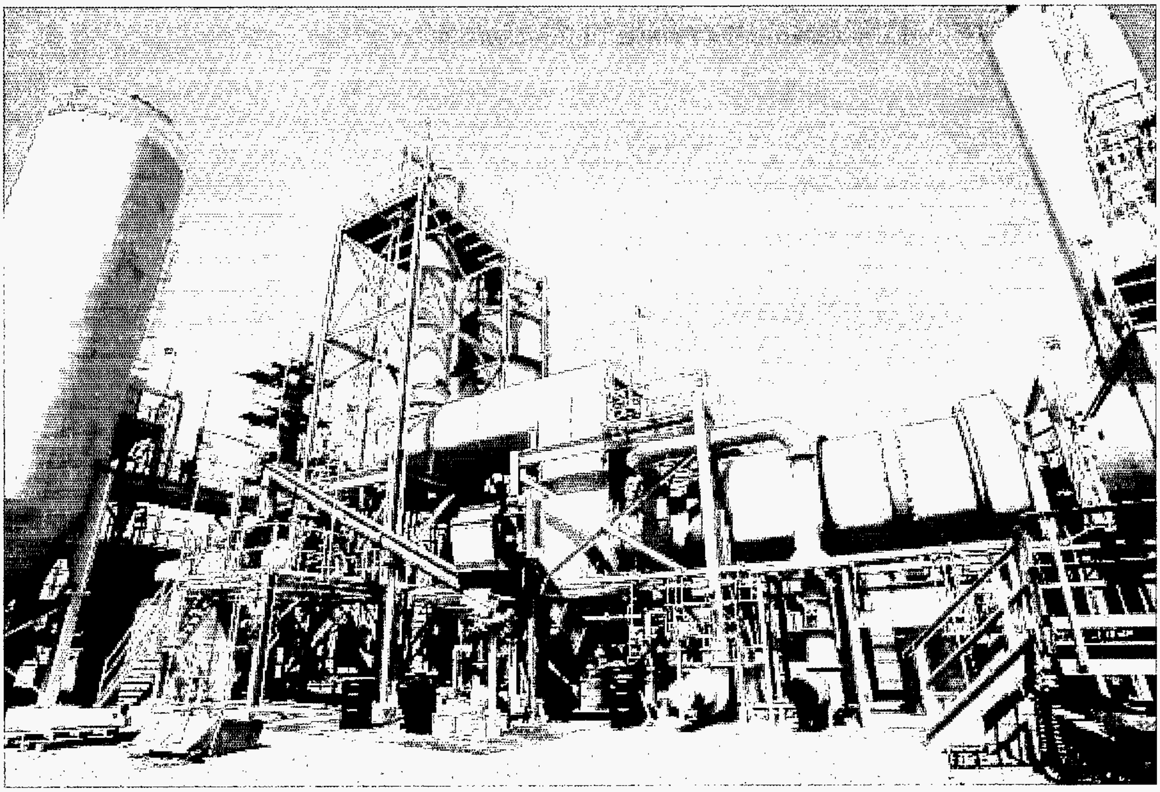

Figure 7. Photograph of the Endesco rotary kiln decontamination demonstration facility at Bayonne, NJ facility that shows the main components of the system. The large horizontal cylindrical vessels are the kiln at the right and the after burner to the left and above that is used to destroy volatile compounds in the exhaust gases from the process.

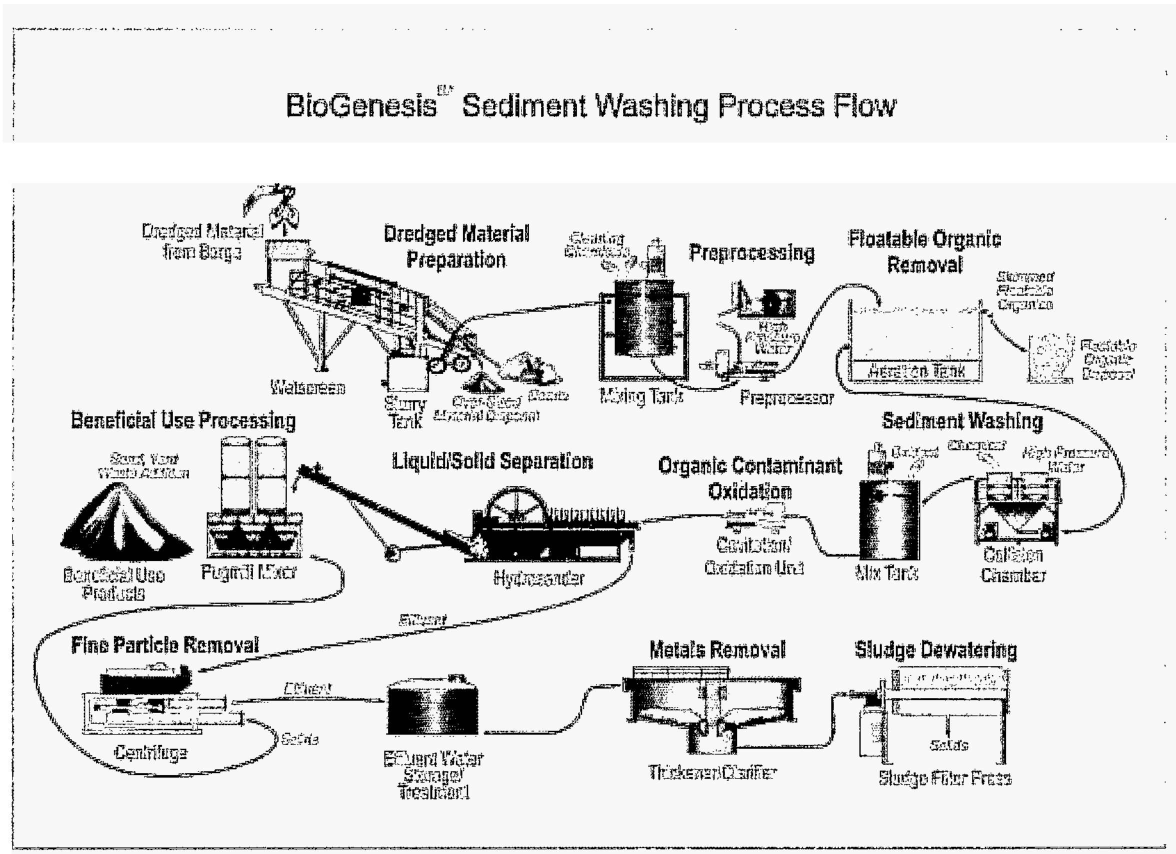

Figure 8. This schematic diagram shows the arrangements of the components of the BioGenesis sediment-washing technology. **A** large-scale demonstration of the system is to be held in Keasby, NJ.

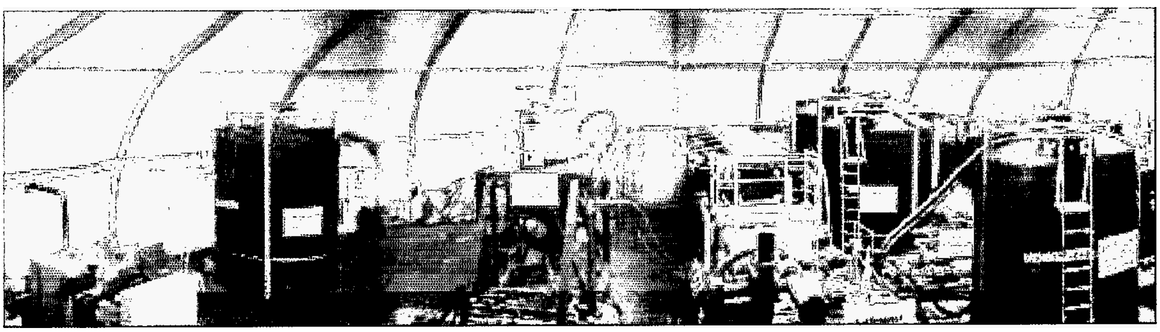

Figure 9. The photograph shows the equipment used in a pilot-scale demonstration of the BioGenesis system performed in Kearny, NJ in 1999.