UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

TECHNOLOGY NEWS AND TRENDS

TECH TRENDS

Ground Water Currents

A newsletter about soil, sediment, and ground-water characterization and remediation technologies

Issue 2 **September 2002**

Sediment Capping Pilot Study Conducted on Grasse River

From July to October 2001, Alcoa Inc. studied the potential for constructing a full-scale subaqueous cap to isolate or reduce polychlorinated biphenyl (PCB) concentrations in sediments, water, and biota of the lower Grasse River near Massena, NY. The pilot study evaluated capping as a remedial alternative for the river and provided information on technical implementation, potential short-term effects of construction, and the cost of the cap. Various capping materials were placed into a 750-foot stretch of the river using different placement techniques. The study found that a cap of acceptable uniformity, thickness, and composition could be placed without significant PCB entrainment from the in-place sediments and without significant impacts to water quality. Optimal results were achieved at this site using a sand/topsoil capping material applied with a clamshell attached to a barge-mounted crane.

The study site consisted of 7 acres located in a stretch of the river containing fine-grained sediment. As a result of previous manufacturing operations, PCB concentrations of up to 11.5 mg/kg were identified in surface sediment. Capping materials were tested in four cells during two project phases.

The first phase was designed to assess a variety of capping materials and application methods in a cell comprising five subcells ranging in size from 19,000 to 38,000 sq ft. Using one to three application lifts, four different capping materials were evaluated at thicknesses of 0.75-1.0 ft: a sand/topsoil (1:1 ratio) mixture, granular bentonite, a sand/soil/bentonite slurry, and AquaBlok™ (a commercial bentonite clay/gravel composite).

Sand/topsoil and AquaBlok materials were installed using a crane-mounted clamshell that released the materials at various water depths. To accomplish this, an equipment barge carrying an 80-ton crane was outfitted with a 2.5-yd mechanical clamshell bucket. Capping materials were prepared at an on-shore staging area and placed on a separate barge. Accurate horizontal control of the bucket, a key element of successful cap placement, was achieved using global positioning system software (WINOPS™) and physical markers on the equipment. A pneumatic broadcasting technique was used to apply the granular bentonite material, and a subsurface tremie method was employed to inject the sand/soil/bentonite slurry. All capping work was cordoned off using a single silt curtain that extended from the water surface to within a few feet of the river bottom.

The second phase of pilot testing was conducted in three 50,000-sq-ft cells. Evaluation criteria included cap coverage characteristics, entrainment of contaminants into the cap, water quality impacts, placement rates, logistic issues, and costs. A cap thickness of 1 ft was targeted for two of the cells, while a thickness of 2 ft was targeted for the third. With the exception of AquaBlok (on which tests were completed during the first phase) capping materials and techniques tested in each of the three cells were similar to those tested during the first phase.

Approximately 900 water samples and 490 sediment samples were collected and analyzed during the study. The results show that over 95% of the PCB concentrations in core samples taken through the pilot cell cap materials were at non-detect levels (below 0.1 mg/kg). Mixing of the

[continued on page 2]

Contents

Sediment Capping Pilot Study Conducted on Grasse River page 1

Food-Grade Oil Injections Used to Stimulate Reductive Dechlorination page 2

In-Situ Chemical Oxidation Pilot Conducted for CVOCs in Fractured Bedrock page 3

Electrochemical Remediation Technologies Remove Mercury in Soil page 5

New Resources for Contaminated Sediment Management page 6

Technical Training Seminars Available On-Line

As part of its continued efforts to provide technical training webcasts, the U.S. EPA Technology Innovation Office (TIO) recently held a "Perchlorate Update" workshop online. This workshop disseminated current information on contamination problems posed by perchlorate. To view the perchlorate workshop materials or participate in future webcast training, visit TIO's CLU-IN website at www.clu-in.org.

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cap material with underlying sediment, where it did occur, generally was limited to the lowest 1-2 inches of capping material. PCB concentrations in water downstream of the cells were below the analytical detection limit (50 ng/L) (Figure 1).

Water quality monitoring during cap placement indicated that no significant releases of PCBs (as shown in Figure 1), total suspended solids, or turbidity occurred during the project. Additionally, post-capping analyses of the site's benthic community showed evidence of recolonization of the capped area within three weeks of the capping completion. Post-capping monitoring of the bathymetry (river-bottom profile) after the first winter shows the cap thickness remains stable.

Unit costs to implement the capping activities (excluding mobilization, silt curtains, design, monitoring, and management) averaged $2.15/sq ft for the 1-ft cap and $3.10/sq ft for the 2-ft cap. Total costs for the study are expected to range from $3.5 million to $4.0 million. Project monitoring will continue at the Grasse River study site throughout 2002.

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Food-Grade Oil Injections Used to Stimulate Reductive Dechlorination

The U.S. Air Force Center for Environmental Excellence (AFCEE) and Air Education and Training Command (AETC) teamed with Altus Air Force Base (AFB) to sponsor field studies on the use of vegetable oil for stimulating in-situ anaerobic bioremediation of chlorinated solvents. Full-scale applications at several military sites indicate that the technology can reduce contaminant concentrations at a lower cost than conventional methods such as pump and treat. Most recently, results from a pilot study at Altus AFB, OK, showed over 90% reduction in trichloroethene (TCE) concentrations within eight months.

The process blends food-grade vegetable oil and surfactants in a high-speed mixer to generate an oil-in-water emulsion with a small droplet size that can be distributed easily throughout the subsurface. The emulsion is injected through permanent wells or temporary direct-push points. Water is subsequently injected to distribute and immobilize the oil. The optimum oil droplet size and surfactant characteristics for each site are determined through laboratory testing.

Historical solvent releases of degreasing agents at Altus AFB resulted in a 5,000-ft-long chlorinated solvent plume with TCE concentrations reaching 78,000 µg/L in the source area. Geology at the site consists of reddish-brown, moderately plastic, sandy clay to a depth of roughly 15 ft, underlain by fractured clayey shale with occasional gypsum layers. The depth to ground water is 8-10 ft below ground surface (bgs). Most ground-water flow and contaminant transport appears to occur through a series of weathered shale fractures located immediately beneath the surficial clay and within a thick gypsum layer approximately 35 ft below grade. Field observations suggest a ground-water velocity approaching 100 ft/yr.

The pilot study is evaluating the use of vegetable oil as a low-cost carbon source for controlling chlorinated solvent migration through enhanced anaerobic bioremediation. A line of six permanent 2-inch PVC wells spaced 5 ft apart was installed perpendicular to ground-water flow approximately 250 ft downgradient from the source area. Over a 4-day period in December 2001, a mixture of emulsified soybean oil, yeast extract, and lactate was injected through each well to form a 30-ft-wide vegetable oil barrier that would stimulate reductive dehalogenation.

Each injection was designed to treat a 6-ft-diameter area that would provide a small overlap between adjacent injection points. To achieve maximum distribution of the treatment mixture in the upper weathered fracture zone, the wells were screened from 8 to 18 ft bgs. The cost of installing the six barrier wells and injecting the mixture was $18,000, or $600/linear ft of barrier.

Monitoring of adjoining wells during the injection process showed that the

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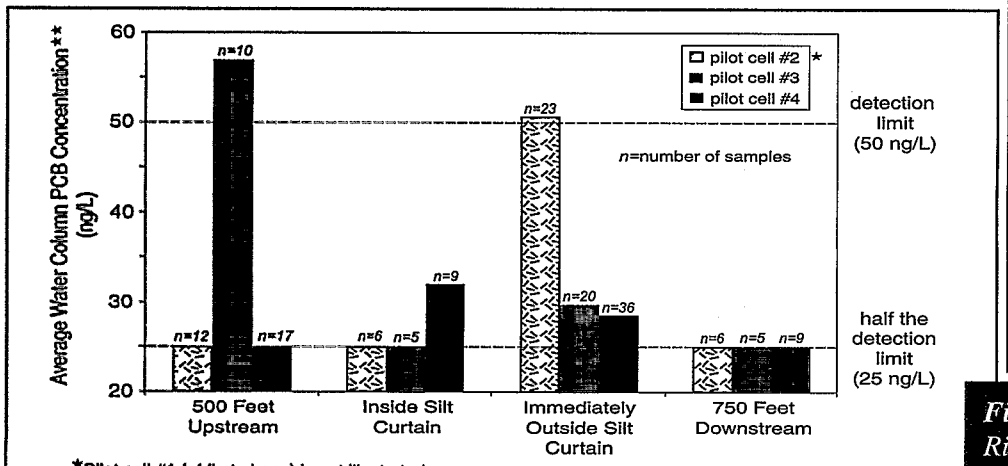

*Pilot cell #1 (of first phase) is not illustrated.
**A value of 1/2 the detection limit (25 ng/L) was assigned to non-detect readings when calculating averages.

Figure 1. *Capping studies on the Grasse River showed minimal impact on surface water quality.*

Electrochemical Remediation Technologies Remove Mercury in Soil

Pilot- and full-scale in-situ remediation projects were conducted at several European sites to evaluate the use of innovative electrochemical remediation technologies (known as "ECRTs") for removal of mercury and other metals from soil. Based on these project results and recent bench-scale testing, the U.S. Department of Energy (DOE) is considering an ECRTs field pilot for removal of mercury and other heavy metals at the National Security Complex (Y-12) near Oak Ridge, TN. Cost reduction is the major driver for DOE to seek alternative cleanup technologies such as these. ECRTs require low levels of electrical energy input compared to other electrical methods such as traditional electrokinetics, joule heating, and vitrification. In addition, ECRTs generally are effective within months, instead of years, and can be performed in-situ or ex-situ.

ECRTs involve the passage of low-voltage/amperage AC/DC current between an electrode pair to create metallic complexes. The ion complexes, as well as ionic metals, are mobilized via the electrokinetic gradient to both the anode and cathode for deposition. These deposits then can be removed and recycled. In contrast to electrokinetics, ECRTs electrically polarize the soil to generate reduction-oxidation (redox) reactions at the pore scale, creating mobile species of the target contaminants that migrate to the electrodes. Field remediation projects suggest that the overall reaction rates of the electrochemical process are inversely proportional to grain size of the soil or sediment undergoing treatment.

These technologies were demonstrated at the Union Canal in Scotland, where an average total mercury (elemental and methyl mercury) concentration of 243 mg/kg was present in the silt of a 1.1-m-deep, brackish-water canal. Over a 26-day period, 220 cubic meters of contaminated silt were treated. Approximately 5.6 kW of electrical power was applied to two electrode pairs placed within the silt at positions parallel to the canal banks. After 12 days of treatment, the average total mercury concentration dropped to 119 mg/kg. The target goal (20 mg/kg) was exceeded by the end of the demonstration, at which time the average mercury concentration was 6.5 mg/kg. A total of 76 kg (168 lbs) of metal deposits, primarily consisting of mercury, accumulated on the electrodes.

Bench-scale testing of mercury-contaminated soil from DOE's Y-12 facility corroborated previous ECRTs field results. The test was conducted on homogenized soil having an average total mercury concentration of 252 mg/kg. Chemical analysis of the soil showed it contained up to 12,000 mg/kg of iron, which created conditions for high electrical conductivity and allowed for laboratory simulation of the ECRTs process.

After 741 hours of testing on the Y-12 soil, the total mercury concentration in soil near the anode increased to more than 530 mg/kg (>120% relative to baseline). In soil near the cathode, the total mercury concentration decreased by approximately 60%. Post-test chemical analysis of the electrodes themselves indicated that the anode accumulated about four times more total mercury than the cathode. The combined chemical data from soil and electrode analyses indicated that mercury was migrating and depositing at both electrodes. This generation and migration of both positive and negative chemical species to their respective electrodes distinguishes ECRTs from classical electrokinetics techniques.

Preliminary engineering cost estimates for ECRTs range from \$135/yd^3 (for volumes of 3,000 yd^3) to \$42/yd^3 (for volumes exceeding 100,000 yd^3). An ECRTs demonstration also is being conducted by the U.S. Army Corps of Engineers, the U.S. EPA Great Lakes National Program Office, and the Minnesota Pollution Control Agency to evaluate its use in removing polycyclic aromatic hydrocarbons (PAHs) in fresh-water sediments of Lake Superior. In addition, the Washington State Department of Ecology and King County, WA, are cooperating with the U.S. EPA in a Superfund Innovative Technology Evaluation (SITE) Program demonstration of the technologies' ability to reduce concentrations of PAHs, mercury, and phenols in marine sediments.

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[continued from page 3]

The 90-m CVOC plume, ranging in width from 20 to 45 m, extended 30 m below the top of the fractured bedrock (35-40 m bgs) prior to ISCO treatment. Baseline sampling found that total CVOC concentrations in two wells exceeded 1,000 mg/L. In the remaining 43 pilot wells, 14 indicated concentrations of 100-1,000 mg/L and 29 indicated less than 100 mg/L. The cross-sectional distribution of CVOCs with depth does not provide evidence of DNAPL pools. Based on the persistence and pattern of CVOC rebound modeled over time, however, DNAPL may exist in poorly connected, soil-clogged fractures near the overburden-bedrock interface.

The ISCO process employed at the NAS involved simultaneous injection of hydrogen peroxide and a ferrous sulfate catalyst into the overburden and fractured bedrock zones. The first phase of injections, which occurred in October 2000, employed 48 injectors spaced at 3 m intervals. Of these, 20 were screened across the saturated portion of the overburden and 28 were screened within the fractured bedrock. Prior to the second (final) injection phase in March 2001, three additional bedrock injectors were installed to improve fracture accessibility. A total of 9,233 liters of peroxide and 28,174 liters of catalyst was injected.

Pilot results indicate that CVOC concentrations in ground water within the bedrock were depressed during and immediately following each phase of injection but rebounded over time at many of the observation points. Figure 3 presents data from two representative observation points. A well outside the treatment zone shows the peroxide and catalyst (represented by iron) equilibriating, thereby allowing the CVOCs and BTEX to rebound. A well in the center of the treatment zone shows the continued persistence of catalyst, which may be artificially depressing the CVOC and BTEX concentrations.

Analysis of monitoring data suggests that a significant amount of dilution occurred due to the addition of peroxide and catalyst (iron). Increased concentrations of dissolved oxygen, as indirect measures of CVOC breakdown and/or the presence of hydrogen peroxide, were observed in 77% of the monitoring wells. Data suggested that 9-12 months were needed for the bedrock system to flush the injected fluids and for CVOC concentrations to re-equilibrate.

Although limited success of ISCO treatment was achieved at the South Weymouth NAS, the pilot refined delineation of the residual contamination source, improved understanding about the interconnectivity of the bedrock fractures, and better defined the applications and limitations of ISCO treatment in a fractured-bedrock setting. To more fully characterize the current aquifer conditions, efforts are underway to further assess the overburden-bedrock interface, the potential DNAPL source areas, and the treatability parameters for alternate remedies. Potential technologies for this site include the injection of alternate oxidants and stimulated anaerobic microbial degradation.

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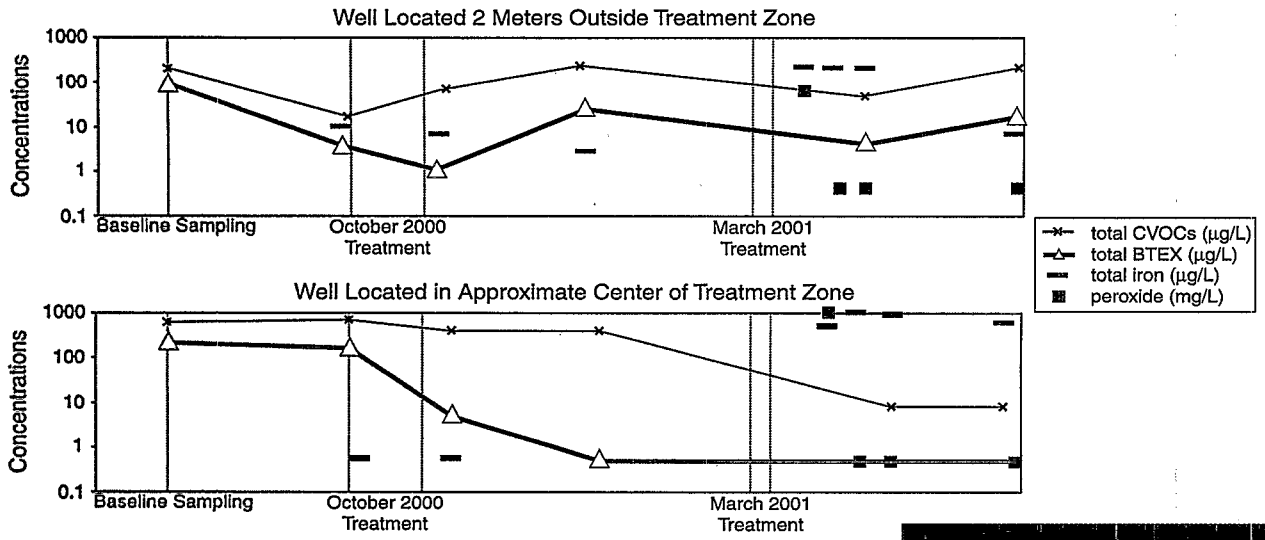
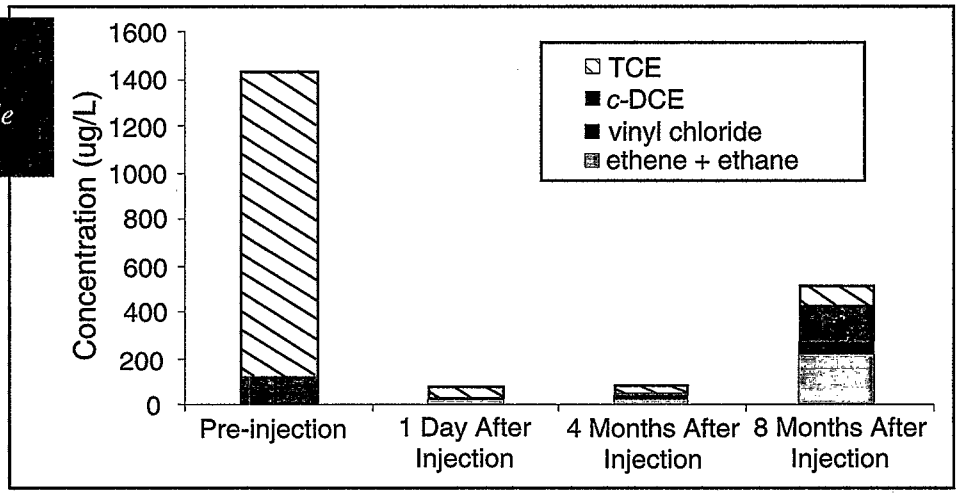


Figure 3. While contaminant reductions were observed in some of the wells, significant rebound occurred in others.

Figure 2. TCE concentrations at the Altus AFB pilot study site dropped immediately after injection of vegetable oil.



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emulsified oil was distributed to a distance of more than 20 ft from the injection points. TCE concentrations dropped immediately after injection due to dilution and/or sorption to the oil. By August 2002, however, TCE and *cis*-dichloroethene (DCE) had rebounded and total ethenes had returned to a level exceeding 90% of the preinjection concentration. These changes indicated that dilution/sorption no longer was significant and that any reduction in contaminant concentrations was due to biodegradation.

Data obtained from one of the six injection wells indicated that the TCE concentration had declined from 1,300 µg/L to 98 µg/L (Figure 2), with 64% of the original TCE and DCE recovered as ethane. Similar TCE reductions were identified in a monitor well located 20 ft downgradient from the barrier, where the concentration dropped from 1,660 µg/L to 20 µg/L. Concentrations of vinyl chloride (an intermediate break-down product) had increased over the 8-month period, indicating that conversion of TCE to ethane was incomplete. Additional monitoring is underway to determine if the barrier width should be increased to achieve complete conversion of vinyl chloride to ethene.

Final results from the pilot test will be used to evaluate potential application of edible oils for full-scale remediation of ground water at Altus AFB. This pilot, as well as previous applications at Dover AFB and Edwards AFB, demonstrate the potential for application of this process in a flow-through barrier for controlling chlorinated solvent migration. Previous commercial applications suggest that this technology also could be used to treat source-area hot spots and to enhance natural attenuation of contaminants. Laboratory studies are planned to evaluate the use of this approach for treatment of other pollutants, including nitrate, perchlorate, chromium, radionuclides, and acid mine drainage.

This project is part of the AFCEE Enhanced Bioremediation Initiative, which is investigating other low-cost substrates such as molasses, direct hydrogen sparging, and bark mulch in a trench application [see the July 2002 issue of *Technology News and Trends*]. The U.S. Air Force, Navy, and Army also are developing a joint Tri-Service guidance manual to outline criteria for selecting appropriate carbon substrates and cost estimating tools in bioremediation applications.

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In-Situ Chemical Oxidation Pilot Conducted for CVOCs in Fractured Bedrock

A recent pilot program undertaken by the Naval Facilities Engineering Command at the South Weymouth Naval Air Station (NAS), MA, illustrates the challenges posed by contaminants in fractured-bedrock aquifers. In-situ chemical oxidation (ISCO) based on Fenton's chemistry was performed to assess the technology's effectiveness in destroying chlorinated volatile organic compounds (CVOCs) in this type of setting. Although initial post-injection sampling showed overall contaminant reductions in ground water, subsequent sampling indicated significant contaminant rebound.

From the 1940s through the 1990s, the 2,800-sq-mi NAS study site was used for vehicle maintenance. As a result, shallow subsurface CVOC releases became mixed with waste oil leaking from an underground storage tank. The site is underlain by approximately 6 m of silty sands, beneath which exists a fractured granite formation. The water table is located approximately 3 m below ground surface (bgs). Ground water flows horizontally in both the overburden and bedrock, which are in direct hydraulic connection.

Slug tests and packer pressure tests in the bedrock treatment zone indicated a hydraulic conductivity ranging from 4.3×10^{-5} to 2.6×10^{-4} cm/s. An average fracture aperture of 156-349 mm was measured, and an effective porosity of 1.03×10^{-3} to 2.86×10^{-3} calculated. Based on these parameters, the bedrock treatment zone was estimated to contain approximately 36,000 liters of water and to require 88-243 days to flush one fracture volume through the zone.

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Technology News and Trends

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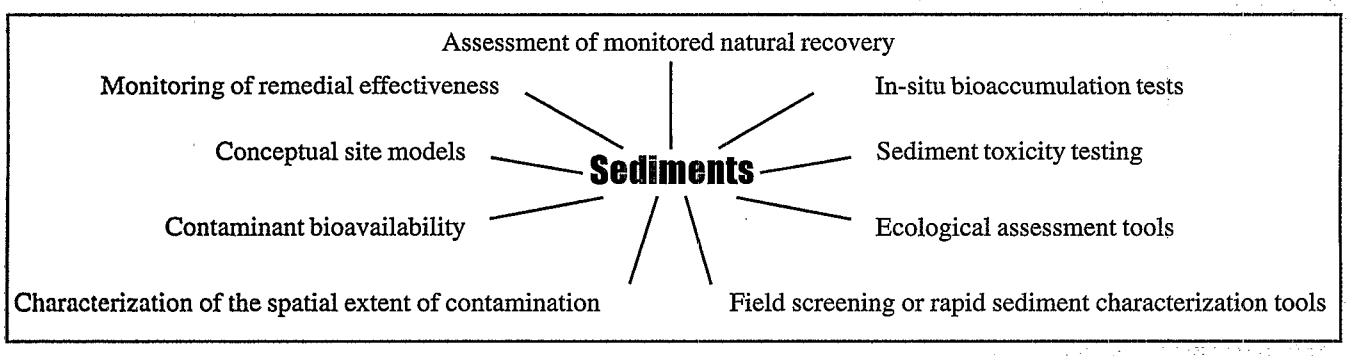
New Resources for Contaminated Sediment Management

Sediment experts representing a variety of research organizations recently collaborated in developing an 88-page white paper, *Critical Issues in Contaminated Sediment Management.* The white paper addresses a range of technical issues:



The white paper was published by the Marine Environmental Support Office of the U.S. Navy (publication number MESO-02-TM-01) and is available on the SedWeb℠ bulletin board at www.sediments.org/sedmgt.html. Other sediment-related information, including on-line discussions and audio web lectures, can be found on SedWeb as a service of the Hazardous Substance Research Centers/ South & Southwest.