

Site Name: Diamond Alkali Superfund Site, Lower 8.3 Miles of the Lower Passaic River (LPR) Operable Unit 2 (OU2)

Location: Essex and Hudson Counties, New Jersey

Type of Site: Superfund site

Contaminants of Concern: Dioxins/furans, PCBs, mercury, total(4,4')DDx, copper, dieldrin, PAHs, lead

Remedy: Dredging to maintain current hydraulic flow capacity, capping, institutional controls, and long-term monitoring and maintenance

Current Site Status: 100 percent design in preparation

Case Study Objectives: Describe the approach and the results of the treatability studies conducted to measure site-specific cap material–porewater and sediment–porewater partition coefficients.

Site Description: The tidal lower 8.3 miles of the LPR OU2, located in Essex and Hudson Counties, New Jersey, are among the most challenging contaminated sediment sites in USEPA's Superfund Program. In 2016, USEPA's ROD determined that an engineered sediment cap would be placed across approximately 700 acres of the lower 8.3 miles after dredging for navigation and flood rise prevention.

Various sediment sampling, water column sampling, fish and invertebrate tissue sampling, and bathymetry surveying have been conducted periodically since 1990. The predesign investigation and treatability study were performed to gather site-specific information for the remedial design. This case study focuses on the treatability studies, which included, among other objectives, field sampling of OU2 river water and sediments and laboratory analyses to evaluate site-specific cap material–porewater partitioning coefficients, as well as sediment–porewater partitioning coefficients for the site-specific COCs.

The treatability studies and predesign investigation have been completed and approved by the USEPA. The 95 percent design has been completed, and several design review meetings were conducted with regulatory agencies during the preparation of the 95 percent design. The 100 percent design is being prepared and is expected to be submitted to regulatory agencies in 2023.

Description of Treatability Study: The LPR COCs include hydrophobic organic compounds (2,3,7,8-tetrachlorodibenzodioxin, PCBs, total (4,4') DDx, dieldrin, and PAHs) and metals (mercury, lead, and copper). Transport of these COCs through the cap is governed in part by how strongly chemicals are bound to the sediment geochemical components and to the cap materials. The engineered sediment caps are being designed using the chemical transport model CapSim. The lowest layer of the cap is a CIL composed of amended sand, which will isolate chemicals from the overlying bioavailable zone. The treatability study measured site-specific partition coefficient values for the native sediment and potential cap materials (sand, topsoil, organoclay, GAC, and PAC) for use as inputs to CapSim. This study compiled literature partition coefficient values for the LPR COCs, filled existing data gaps in the literature by measuring partition coefficient values for a range of organic and inorganic chemicals and cap materials reflective of OU2 conditions, measured site-specific sediment–porewater partition coefficient values, and recommended values for use in the CIL design informed by site-specific measured partition coefficients and values from ranges in the literature.

Cap Material Treatability Testing Approach: Sediment cores and surface water samples at mid-water depth were collected from five different locations representative of the OU2 concentrations (**Figure 1**). Sediment cores were homogenized and pre-screened to remove any large debris. OU2 sediment and surface water were mixed (**Figure 2**).



Figure 1. Sediment core collection at LPR.



Figure 2. Sediment and water mixture to prepare synthesized porewater.

Once the sediment consolidated, the supernatant was passed through a 0.45 μm filter to prepare synthesized porewater for use in the bench-scale sorption isotherm tests. The synthesized porewater was prepared to match OU2 DOC levels and the range of OU2 COC concentrations in sediment to provide partition coefficients representative of OU2 conditions. Baseline DOC results in synthesized porewater were compared with the average DOC measured in the sediment interstitial water. Additional organic carbon, using the Suwannee River NOM standard, was spiked into the synthesized porewater to achieve the target DOC to perform the tests with representative OU2 DOC concentration. The synthesized porewater was spiked at five concentration levels for organic and inorganic COCs to develop an isotherm. The spike levels covered a wide range of concentrations spanning the range of concentrations measured in OU2 sediments. In addition, the lowest spike concentrations were calculated based on the amount of material added and expected sorption, such that the final dissolved concentration of the spiked COC would be greater than the analytical laboratory-specific quantitation limits and environmental baseline concentrations estimated in the porewater.

The effect of competitive sorption and sorption attenuation by NOM was taken into account by the presence of several organic and inorganic COCs and matching OU2 DOC levels in the synthesized porewater. The pH in the synthesized porewater was maintained within the range observed at OU2.

Description of Cap Material Treatability Study (continued):

Polyethylene passive samplers for use in the sorption isotherm test were precleaned and preloaded with performance reference compounds (**Figure 3**). Passive sampler strips were added to all test jars. Sodium azide was added to each test jar to inhibit biological activity during the performance of the test. Five different cap materials were added to the treatment jars (**Figure 4**). For QA/QC, control jars were also prepared, and the tests were conducted by preparing two separate replicate jars for each COC concentration level. All jars were kept under anoxic conditions. Pre-test concentrations in the cap materials and passive samplers were measured. Pre-test aqueous concentrations in the control jars were measured. Post-test passive samplers and aqueous samples were collected for analysis from all test jars, including treatment and control jars. See **Figure 5** for a summary of the samples collected as part of the cap material treatability testing.

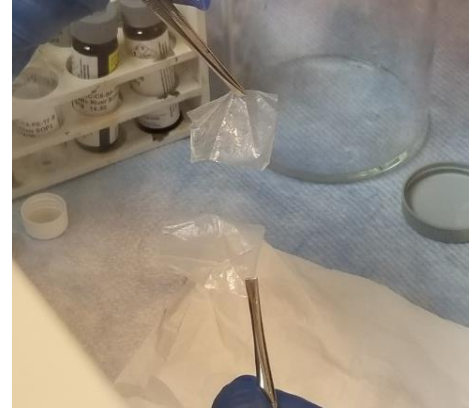


Figure 3. Polyethylene sampler.

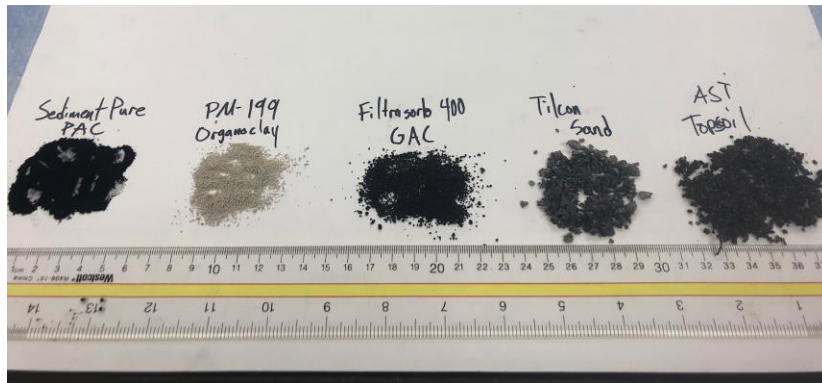


Figure 4. Cap material used in the treatability testing.

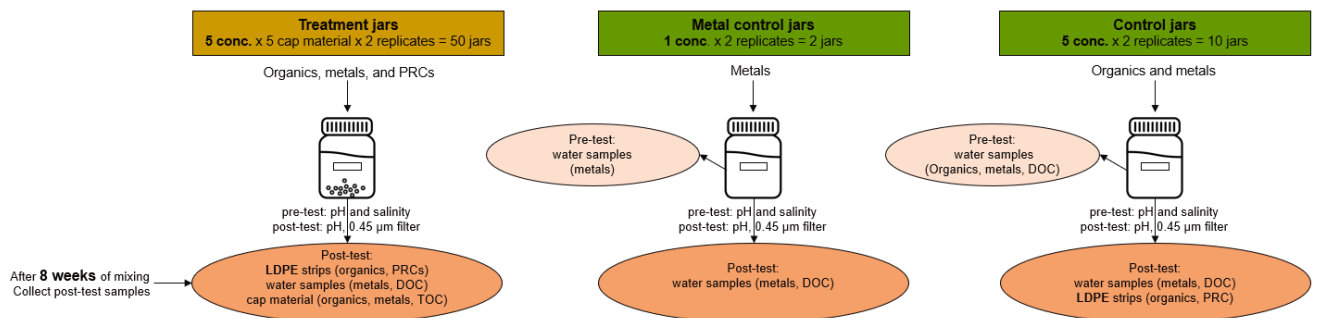


Figure 5. Samples collected as part of the cap material treatability testing.

Description of Cap Material Treatability Study (continued):

Equilibrium porewater concentrations were obtained for organic COCs using passive sampling data and inorganic COCs using the results of direct analysis in the aqueous samples. A mass balance approach was used to calculate the equilibrium concentration in the cap material for organic and inorganic COCs. Once plotted against each other, cap material–porewater results were fit to linear partitioning and Freundlich equations. The trends in the data and fitting parameters were reviewed, and the fit that best explained the sorption behavior was selected.

Sorption behavior to the five different cap materials of most COCs were linear within the range of OU2 COC concentrations, except for activated carbon where nonlinear sorption behavior was observed for several COCs. Most of the cap material–porewater partition coefficients were within the literature range for COCs with available information in the literature, particularly for organic COCs that were less dependent on site-specific parameters. An extensive review of the literature was conducted for cap material–porewater partition coefficients for each COC, and sensitivity analysis was conducted to provide a bound on the measured site-specific partition coefficients.

The approach to recommend cap material–porewater partition coefficient values for use in the CIL design was as follows:

- If the site-specific measured value was within or close to the literature range, the site-specific measured value was recommended for use in the CIL design.
- If the site-specific measured value was outside the literature range, an average of the measured value, the low end, and the high end of the retained literature values was recommended for use in the CIL design.

For inorganic COCs, the site-specific measured values were recommended for use over the literature values because the measured values reflect OU2 conditions, except when the site-specific measured value was significantly different from the literature range. In this case, an average of the measured value, low end, and high end of the retained literature values was recommended for use in the CIL design.

Sediment Treatability Testing Approach: Sediment cores and surface water samples at mid-water depth were collected from different locations throughout OU2. Sediment cores for the inorganic analysis portion of the work were sealed and immediately frozen.

Porewater measurement for freely dissolved concentrations of the organic COCs was conducted through passive sampling techniques. The homogenized sediment collected from each location was mixed with OU2 surface water collected from the same location in a 1-liter amber glass jar. Sodium azide was added to each test jar to inhibit biological activity during the performance of the test. Polyethylene passive samplers were precleaned and preloaded with performance reference compounds prior to being deployed in the equilibrium test jars. Bench-scale equilibrium tests were conducted over a period of 2 months (**Figure 6**). Subsamples of the homogenized sediment were collected and analyzed for organic COCs and TOC. Passive samplers were retrieved and analyzed at the end of the 2-month equilibration period. For QA/QC, duplicate samples were included in the analysis.



Figure 6. Equilibrium study for the porewater measurement of the organic COCs.

Description of Sediment Treatability Study (continued):

Porewater concentrations of the inorganic COCs were measured through direct analysis of the porewater extracted from homogenized sediment cores handled anoxically in a glove box (**Figure 7**). Porewater was extracted through centrifugation and filtration techniques using a 0.45 μm filter to separate the particles from the dissolved phase. The porewater samples were analyzed for inorganic COCs, pH, and DOC. The sediment samples were collected and analyzed for inorganic COCs and TOC. For QA/QC, duplicate samples were included in the analysis.

The ratio of the equilibrium sediment concentration to the equilibrium porewater concentration was calculated to obtain partition coefficient values for each of the COCs at each sampling location. Partition coefficient values were plotted along the 8.3-mile length of OU2; for the majority of COCs, no spatial relationships were observed. Therefore, an OU2-wide average of the measured sediment-porewater partition coefficient values that reflect the site conditions were recommended for use in the CIL design.



Figure 7. Sediment core handling for the porewater measurement of the inorganic COCs.

Conclusions:

The main conclusions include the following:

- Site-specific partition coefficient values for all COCs were determined for sediment and select cap materials.
- Sensitivity analysis and literature review were used to inform the selection of reliable values for design.
- Refining the mass balance approach by direct measurement of DOC-porewater partition coefficients and COC mass in the synthesized porewater at time zero would improve the ability to achieve mass balance closure.

References:

The treatability studies and predesign investigation have been completed and approved by USEPA and are available online at:

<https://sharepoint.ourpassaic.org/Public%20Documents/Forms/AllItems.aspx>.