

A.1 Technology Name

Polymeric Sampling Devices

A.1.1 Source

Garza-Rubalcava, Uriel, Alex V. Smith, Courtney Thomas, Marc A. Mills, W. Andrew Jackson, and Danny D. Reible. 2023. Long-Term Monitoring and Modeling of PAHs in Capped Sediments at the Grand Calumet River. *Environmental Pollution* 328:121633. <https://doi.org/10.1016/j.envpol.2023.121633>.

A.1.2 Summary

Media:	Porewater (Sediment and Cap)
Study Type:	In-situ
Technology:	Polydimethylsiloxane (PDMS)
Peer Reviewed:	Yes
Publication Date:	April 2023

A.1.3 Site Description

- The study conducted at the Grand Calumet River in Indiana, USA, involved a seven-year monitoring of polycyclic aromatic hydrocarbons (PAHs) in a remedial cap.
- Remediation involved dredging approximately 585,000 cubic yards of sediments and placing a cap made of about 15 cm of organophilic clay and 30 cm of sand. The remedial action started in 2011 and completed by April 2012.
- The objectives were to (1) evaluate the cap performance over time; (2) understand the processes affecting the transport and degradation of the PAHs. Processes considered included groundwater upwelling, bioturbation of the surficial sediments, sorption-related retardation (especially in the organophilic clay), and degradation of contaminants.
- Polymeric passive sampler (PPS) consists of a 500 µm diameter glass rod coated with a 37.5 µm layer of polydimethylsiloxane (PDMS), which was prepared as a segment of 90 cm and placed inside a narrow slit in a stainless-steel rod (a modified version of the PushPoint sampler).
- The PPS units were deployed for 28-days to measure porewater profiles of PAHs at 14 Long-Term Monitoring (LTM) stations over three consecutive years (2012-2014) and again in 2019.
- Sediment cores were collected in 2013 and 2019 to measure bulk concentrations of PAHs and to evaluate changes in the cap thickness.
- In 2019, seven sediment high-resolution passive profilers (sHRPPs) were deployed to measure the interstitial concentration of chloride and sulfate, and to estimate pore water velocity.
- Non-equilibrium correction was estimated using a transient transport model around the cylindrical fiber calibrated using performance reference compounds (PRCs) (Shen and Reible, 2019).

A.1.4 Remedial Phase

Post Remedy

A.1.5 Outcome

Effectiveness of the Cap: The cap was effective in maintaining a physical barrier between contaminated sediments and surface water. Data showed that bulk concentrations of PAHs in the cap were between two and three orders of magnitude lower than in native sediments below the cap. However, differences in porewater PAH concentrations were less pronounced. The average porewater concentrations in the cap were lower than in the native sediments by a factor of at least 7 for phenanthrene, 3 for pyrene, and 1.5 for benzo[a]pyrene.

Changes in PAH Concentrations Overtime: When compared to baseline levels measured between 2012 and 2014, the depth-averaged porewater concentrations in sediments after seven years (2019) showed a reduction of 80% for phenanthrene and 53% for pyrene, but no change for benzo[a]pyrene. For porewater in the cap layer, over the same period, phenanthrene concentrations decreased by 73%, pyrene decreased by 29%, but benzo[a]pyrene increased by 2-fold.

Transport and Degradation Mechanisms: Inorganic anions and estimates of pore water velocity along with measurements of PAHs were used to model the fate and transport of contaminants. The modeling suggested that degradation of phenanthrene and pyrene in the cap is faster than migration, thus the cap is expected to be protective of the sediment-water interface indefinitely for these constituents. Conversely, no significant degradation was observed for benzo[a]pyrene and the contaminant is expected to reach equilibrium in the cap layer over approximately 100 years, assuming sufficient mass of benzo[a]pyrene in the sediments and absence of clean sediment deposition on the surface.

A.1.6 References

Shen, Xiaolong, Reible, Danny, 2019. An analytical model for the fate and transport of performance reference compounds and target compounds around cylindrical passive samplers. Chemosphere 232, 489–495. <https://doi.org/10.1016/j.chemosphere.2019.05.198>.