PlumeStop® Technical Bulletin 4.1

Regeneration of Sorptive Capacity

Quick Reference:

- PlumeStop binding site bio-regeneration
- Extended functional longevity

Background

PlumeStop® Liquid Activated Carbon™ is composed of very fine particles of activated carbon (1-2 μm) suspended in water through the use of unique organic polymer dispersion chemistry. Once in the subsurface, the material behaves as a colloidal biomatrix, binding to the aquifer matrix, rapidly removing contaminants from groundwater, and expediting permanent contaminant biodegradation.

Wide-Area Dispersive Distribution

Unlike any other sorbent technology, PlumeStop can be installed in the subsurface through dispersive flow from low-pressure injection (without fracturing the formation), providing a wide-area thin-film coating of the aquifer matrix. It does not create preferential flow pathways, plug the formation, or compromise monitoring wells through extreme carbon loading, as is often the case with pressure-emplaced powdered activated carbon products.

More information on low-pressure ease of distribution and dispersive emplacement of PlumeStop can be found in PlumeStop Technical Bulletin 1.1: Distribution through a Permeable Medium.

Rapid Removal of Contaminants from Groundwater

PlumeStop rapidly sorbs organic contaminants from aqueous solution within the timescale of hours. Pollutants partition directly into the PlumeStop particles that are sorbed to the soil formation, thereby removing the pollutants from groundwater. Contaminant advection in the aqueous phase is therefore eliminated, and partitioning into the vapor-phase is also reduced (Henry's Law). Results can be dramatic, with groundwater cleanup objectives often met within days of PlumeStop application.

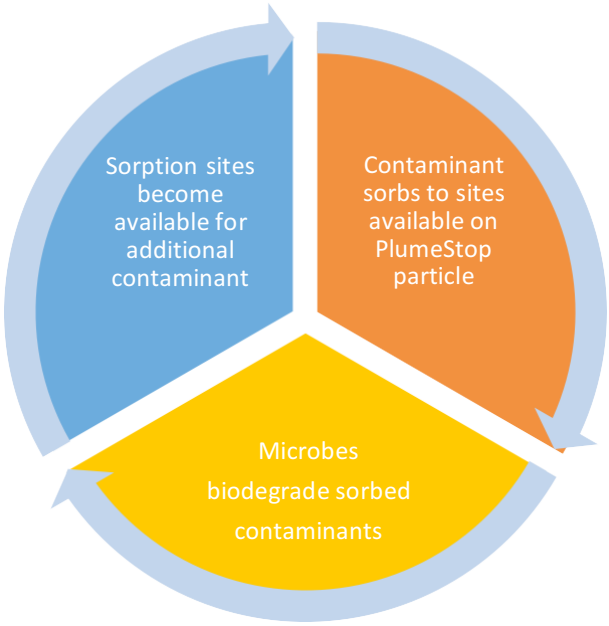
Acceleration of Contaminant Biodegradation

Once sorbed to the soil and with contaminants partitioned onto its surface, PlumeStop is colonized by contaminant-degrading bacteria. These may be naturally present or applied as an inoculum. The concentration of the contaminants and the degradative microflora on the PlumeStop surface reduces mass-transfer kinetic constraints and supports greater speed and efficiency of degradation compared to solution-phase bioremediation.

The net result is a substantial increase in the instantaneous rate and extent of contaminant destruction. Further information on post-sorption biodegradation and rate acceleration by PlumeStop can be found in PlumeStop Technical Bulletin 3.1: Post-Sorption Contaminant Biodegradation.

Regeneration *In-Situ*

Within the subsurface, the sorptive capacity of PlumeStop that has coated the aquifer pore structures continues to regenerate *in situ* by the continual cycle of contaminant sorption and biodegradation.



This cycle consists of three events:

- Dissolved-phase contaminants partition out of the groundwater and are concentrated on the PlumeStop particles.
- Opportunistic contaminant-degrading microbes colonize the PlumeStop to form the biomatrix.
- Biodegradation of contaminants within the biomatrix frees up sorption sites, allowing further partitioning of contaminants out of the groundwater.

As a result of this on-going regeneration of the PlumeStop biomatrix, each application of PlumeStop remains functional for an extended / indefinite period of time.

Data Supporting the *In Situ* Regeneration

To demonstrate the *in situ* regeneration of PlumeStop, a laboratory study was undertaken that compared the removal of perchloroethene (PCE) from a biotic soil/water slurry treated with PlumeStop versus two sterile soil/water slurries: one PlumeStop treated and the other a soil-only control. Throughout the study, the aqueous-phase and total-system PCE concentrations were monitored following cycles of PCE spikes and equilibration.

Test Procedure

For the biotic PlumeStop treated conditions, twenty-seven microcosm samples were prepared in 8 oz amber serum bottles sealed with Mininert™ valves (Figure 1). Each bottle contained site soil (20 g), PlumeStop (50 mg/L), microbial consortia (1 x 10^6 cells/mL Dehalococcoides ethenogenes), and sodium lactate as an electron donor to promote biological reductive dechlorination (1,000 mg/L). Similarly, the sterile control samples were prepared with autoclaved site soil (20 g), sodium lactate (1,000 mg/L), and sodium azide (200 mg/L), which was added as a biocide to inhibit biological activity. PlumeStop (50 mg/L) was also added to the PlumeStop treated sterile control.

Figure 1. Experimental set-up - test microcosms

The experiment was initiated with the addition of 2.3 mg of PCE to each bottle.

All bottles were placed on an orbital shaker at room temperature throughout the entire experiment. After 24 hours, three samples from each of the three conditions (biotic PlumeStop treated, sterile PlumeStop treated, and sterile soil-only control) were chilled prior to removing a 1 mL aliquot for headspace analysis by Gas Chromatography-Electron Capture Detector (GC-ECD) to determine the PCE concentration in water. The same

sample bottles were then sacrificed and subjected to a 48-hour total system extraction with hexane. The hexane extract was analyzed by GC-ECD to give the total mass of PCE within each bottle, which includes both the aqueous-phase and the sorbed-phase (soil and PlumeStop) PCE.

After two weeks, the same sampling procedure described above was repeated on another set of sample bottles, three from each condition. At the same time, all remaining sample bottles were spiked with an additional 2.3 mg of PCE and 25 mg of sodium lactate. The freshly spiked bottles were allowed to equilibrate for six hours before an additional set of sacrificial bottles were sampled and analyzed in order to establish a new post-spike baseline. The identical procedure described above of analyzing–spiking–analyzing was repeated at the four- and six-week time points of the experiment, giving a total of four complete cycles of spiking and analyzing. Two additional PCE analysis-only cycles (no spikes) were also conducted at the eight and ten-week time points.

Results and Discussion

The aqueous-phase PCE concentrations of the soil-only sterile control vials indicated a PCE increase in the aqueous phase at the beginning of the experiment and with the addition of each successive PCE spike (Figure 2). Lower initial concentrations for the two PlumeStop treated conditions compared to the sterile soil-only control suggested rapid sorption of the PCE to PlumeStop in the early phase of the experiment. However, with successive PCE spikes, a build-up of PCE in the aqueous phase was also observed for the sterile PlumeStop treated control, while the concentrations in the biotic PlumeStop treated samples remained overall very low.

The lower aqueous phase concentrations of PCE in the biotic vs. sterile PlumeStop treated samples support *in situ* regeneration of PlumeStop's sorptive capacity by biodegradation. In the sterile samples with PlumeStop, continued addition of PCE to the system resulted in saturation of the PlumeStop sorption sites and an increase in aqueous phase PCE concentrations. In the biotic PlumeStop treated samples, degradation of the sorbed PCE regenerated the sorption sites, thereby allowing the aqueous phase concentrations to remain low throughout the experiment.

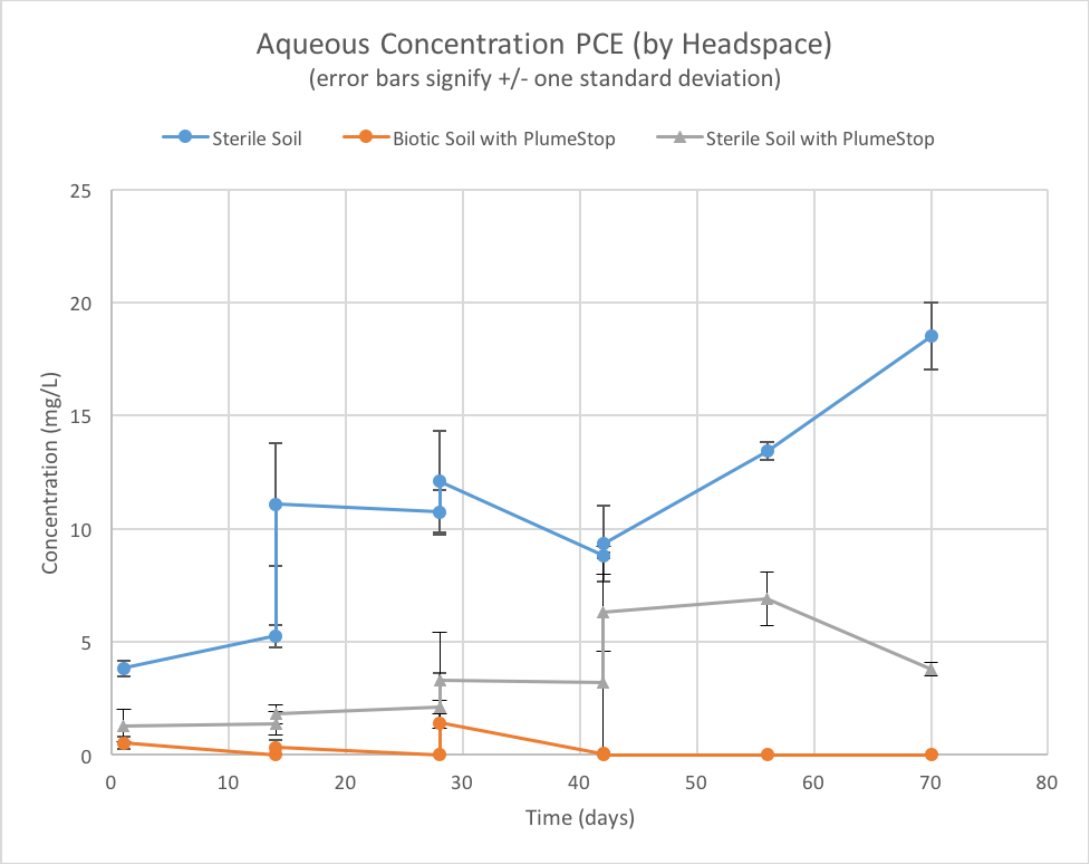


Figure 2. Comparison of dissolved-phase PCE concentrations upon cumulative loading.

Data from the total system extractions (Figure 3) confirmed rapid degradation of the added PCE in the biotic PlumeStop-amended vials; at the time of each sampling, less than 10% of the added PCE remained in the biotic PlumeStop samples prior to re-spiking with additional PCE. Conversely, in the sterile control vials both with and without PlumeStop, the total mass of PCE in the system was retained following each additional PCE spike, indicating that there was no destruction of the contaminants under those conditions. The degradation observed in the PlumeStop-amended vials serves to regenerate the sorptive capacity of PlumeStop, as observed in the aqueous-phase concentrations discussed above. Together, the aqueous-phase and total system extract data clearly support the ability of PlumeStop to maintain a continual cycle of contaminant sorption and degradation.

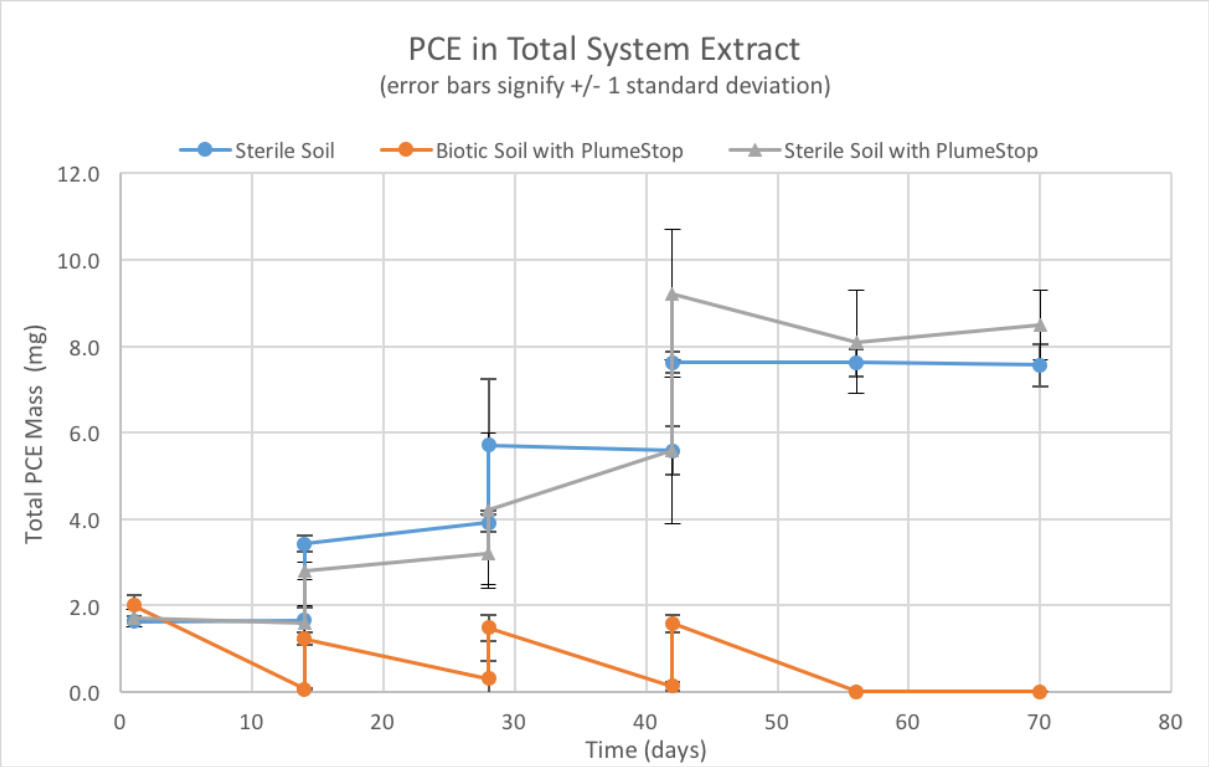


Figure 3. Comparison of PCE mass on cumulative loading– total system extracts.

Summary and Conclusion

The laboratory test clearly demonstrated the ability of PlumeStop to regenerate *in situ*:

- PCE rapidly partitioned onto the PlumeStop particles in the early phases of both the biotic and sterile Plumestop treated samples, removing PCE from the aqueous phase.
- Continued addition of PCE resulted in increasing aqueous-phase concentrations in the sterile samples containing PlumeStop as a result of the sorption sites becoming saturated.
- In the biotic PlumeStop samples, the sorbed PCE was degraded, leaving negligible PCE in the system (sorbed-phase or aqueous-phase).

- After sorbed PCE was degraded, the regenerated PlumeStop particles were again able to sorb additional PCE from solution, thereby providing capacity for continued contaminant sorption and degradation.

The demonstrated regeneration of PlumeStop's sorptive capacity during contaminant biodegradation suggests extended, if not indefinite, treatment longevity.