

Technical Bulletin

OSourceStop[™]

A High Concentration Colloidal Activated Carbon Product for Immobilizing PFAS at the Source

SourceStop: A High-Concentration Colloidal Activated Carbon Product for Immobilizing PFAS at the Source

SECTION 1.0

Quick Reference:

Topic

SourceStop: A High-Concentration Colloidal Activated Carbon Product for Immobilizing PFAS at the Source

Relevant Technologies

OSourceStop[®]

PLUME STOP

Date Published July 20, 2022 Awareness of the presence and impacts of per and polyfluorinated alkyl substances (PFAS) in the environment is growing steadily, and there are increasing efforts to mitigate these impacts worldwide. PFAS are a class of fully or mostly fluorinated compounds used in consumer products and industrial applications specifically for their unique properties of being simultaneously repelled by water and oils. The strength of the carbon-fluorine bonds in these molecules, partially responsible for their desirable commercial properties, leads to PFAS being extremely persistent in the environment.

PFAS have been released to the environment primarily through industrial manufacturing and the use of PFAS-containing firefighting foams. These PFAS releases often occur at or near the surface and deposit onto the shallow soils. Precipitation events induce PFAS leaching downward through the vadose zone. Over time, the PFAS present on soils can migrate deep enough to reach groundwater, leading to PFAS mass discharge and the evolution of a dissolved-phase plume.

To date, PFAS are believed to be almost entirely resistant to biodegradation, and the available commercial methods for their degradation are inefficient or highly energy intensive. Alternatively, a practical and sustainable approach to address these PFAS source areas and manage the risk of PFAS in the environment is by stabilizing or immobilizing PFAS *in situ*. Activated carbon is able to immobilize PFAS due to its hydrophobicity and high surface area. PFAS leaching can occur rapidly during precipitation events, suggesting the importance of adsorbing PFAS with high time efficiency to halt their continued vertical migration. SourceStop™, a highly concentrated colloidal activated carbon product applied to the base of PFAS source zone treatments, has been developed specifically for this purpose.



SECTION 2.0 Technology Description

SourceStop[™] is a high-concentration Colloidal Activated Carbon (CAC) product formulated to restrict the vertical migration of PFAS in the soil beneath source zones where the chemicals were initially discharged into the environment. SourceStop is comprised of carbon particles milled to 1 to 2 microns size and contained in a water-based colloidal suspension. The colloidal nature of the product ensures it distributes evenly in the subsurface, coating the matrix material and forming a filter with an immense estimated surface area, resulting in both rapid and sustained contaminant capture.

Even though SourceStop mainly removes PFAS due to the high sorption capacity and affinity provided by activated carbon properties, its tiny particle size takes great advantage in removing PFAS rapidly as well as coating the target media (i.e., soil) more evenly, compared to other commercially available activated carbons. Powdered activated carbon (PAC), a well-developed and commercially available activated carbon type, predominantly has a particle size of 0.045-0.180 millimeters (mm). While PAC can provide strong sorption capacity to immobilize PFAS in vadose zones after <u>direct mixing it with PFAS-impacted soil</u>, its performance and application can be limited by its size. PAC can be more than 100 times larger than CAC, resulting in capturing leaching PFAS during heavy/ very heavy rain events less efficiently and poor distribution to the soil layer by direct pushing. **Reference 1**

SourceStop is applied *in situ*, via direct mixing or spray-application at the base of a PFAS source zone treatment. Its application is combined with additional treatments at or near the surface to immobilize PFAS and prevent water infiltration. SourceStop is used to create a CAC barrier between the treated soils and surrounding untreated material and to penetrate underlying soils to coat the vertical flow-paths and prevent any further infiltration of residual PFAS.

Application of SourceStop is a method used to enhance the attenuation of PFAS **Reference 2** by increasing the native soil's capacity to sorb and retain PFAS in place. A thin layer of SourceStop applied to the base of a source zone treatment area reduces PFAS leaching to groundwater by several orders of magnitude, as shown in an experimental simulation of a SourceStop basal treatment subjected to a prolonged period of heavy/very heavy rain events.



SECTION 3.0 Proof of Concept Experiment:

Simulation of Activated Carbon Treatment Layer Beneath a PFAS Source Zone

A lab-scale simulation was performed to test the ability of a layer of activated carbon (PAC or SourceStop) to retard PFAS migration in the vadose zone during heavy/very heavy rain events. At typical Aqueous Film Forming Foam (AFFF)-impacted sites, PFAS concentrations tend to be highest near the surface, decreasing rapidly with depth. To match a typical PFAS distribution, the experiment arranged soil layers in the test cells with a high-concentration PFAS layer placed atop low-concentration, PFAS-impacted soils obtained from a project site.

In most cases, REGENESIS' source zone immobilization projects will include additional treatment of PFAS-impacted soils above the zone where SourceStop will be applied (i.e., the bottom interval of a PFAS source treatment volume). This test does not account for additional source treatment and instead simulates an extreme condition of highly concentrated PFAS leaching from untreated, ground surface/shallow soils through the vadose zone to a hypothetical groundwater surface. As performed, the retardation effects of a typical activated carbon application were isolated from any additional soil/surface treatments likely to be conducted.

All soils used in the experiment were 'native,' collected from an area of a project site slightly impacted by AFFF. The soils were sieved to remove material larger than 2 mm.

Cumulative leaching rates for activated carbon treated cells (SourceStop/ PAC) and an untreated control cell were determined according to the following experimental setup and as illustrated in **Figure 1**:



Figure 1

Soil setup for control, SourceStop and PAC treated test. Both SourceStop and PAC treated cells received 10 g of net carbon weight.

Diagram of Control, SourceStop, and PAC Test Configuration



- Each test cell was filled with 900 grams (g) of site soil slightly impacted by AFFF. The total extracted PFAS concentration for this site soil was 25.2 nanograms per gram (ng/g).
- 2. In the SourceStop treatment cell, 32 g of CAC were spray-applied evenly on the site soil. No SourceStop was applied to the control cell.
- 3. In the PAC treatment cell, 10 g of PAC (same net carbon weight as SourceStop-treated cell) were applied on top of the site soil.
- 4. High concentration PFAS soil was prepared by spiking site soil with a legacy C8-based AFFF concentrate. The total extracted PFAS concentration was 14,554-25,107 ng/g, approximately 600-1,000 times more highly concentrated than the native site soil.
- 5. 100 g of the AFFF-spiked soil was added to the top of the control, SourceStop treated, and PAC treated cells.
- 6. Approximately one centimeter (cm) of coarse silica sand was placed on top of the AFFF-spiked soil for these three tests to ensure the simulated rainwater feed was distributed evenly across the soil during precipitation.

- Synthetic Precipitation Leaching Procedure (SPLP) solution (pH=5, per EPA SW846 Method 1312 established protocol). Reference 2 was applied to each test cell at a rate of approximately 8.5 mm/hour, Footnote 1 for two-hour intervals, at a frequency of three times weekly. The total simulated rainfall for the test duration was approximately 102 inches.
- 8. Samples were collected and analyzed for PFAS from the effluent leaching beneath each test cell. All effluent samples were sent for PFAS analysis per EPA 537 LC/MS/MS Method (Eurofins, Lancaster). In the SourceStop cell, black-colored water was observed until up to 75 inches of cumulative precipitation. Approximately 86% spray-applied CAC was retained on the soil of the SourceStop test cell as determined from the carbon concentrations in the effluent samples. Centrifugation was performed to remove the small amounts of suspended carbon from these samples prior to shipping. The effluent from both the control test cell and PAC treated cell remained clear throughout the experiment.
- Sample results were plotted for the three test cells comparing cumulative leaching percentage from the spiked soil cells vs. cumulative precipitation.

^{1.} With 8.5 mm/hr rainfall, it is defined as "very heavy rain" by USGS. (Rainfall calculator, metric-How much water falls during a storm? USGS Water Science School). Since the simulating rainfall shows slightly different precipitation rate each time, sometimes it can be only 8 mm/hr, which is defined as "heavy rain" by USGS. Hence, "heavy/very heavy rain" is used throughout this Technical Bulletin.



SECTION 4.0 Results and Discussion

Effluent samples from the entire soil zone were collected and analyzed for PFAS concentrations throughout the experiment. The effluent samples collected from beneath the control, SourceStop-treated, and PAC-treated cells represent the amount of vertical PFAS migration through the vadose zone to a hypothetical groundwater surface at the effluent collection point.

The leaching percentages of perfluorooctanoic acid (PFOA), perfluorobutane sulfonic acid (PFBS), and perfluorooctane sulfonic acid (PFOS) from AFFF-impacted soil during heavy/very heavy rain events are shown on Figure 2. PFOA, PFBS, and PFOS are given specific attention since:

- the USEPA is moving forward to have PFOA and PFOS maximum contaminant levels (MCLs) for drinking water,
- only PFOA, PFBS, and PFOS are available for calculating USEPA Regional Screening Levels (RSLs) in tap water and soil,
- these three PFAS compounds have notification levels in groundwater under the National Defense Authorization Act, and
- the USEPA is poised to add PFOA, PFOS, and PFBS (plus GenX) as Hazardous Constituents under the Resource Conservation and Recovery Act (RCRA). Footnote 1

 8 Basis of Regulations – PFAS – Per- and Polyfluoroalkyl Substances (itrcweb.org); GenX is not commonly detected in AFFF-impacted areas. Therefore, GenX is not discussed here.

SECTION 4.1

Leachability Results for PFOA, PFBS, and PFOS

The cumulative leaching of PFOA, PFBS, and PFOS from AFFF-impacted soil during simulated rainfall is shown in Figure 2. Almost all PFOA, PFBS, and PFOS added to the upper 100 g soil layer leached out from untreated soil as the cumulative leaching percentages are 131%, 101.7%, and 91.2%, respectively. Figure 2A Over 100% cumulative leaching from control was observed for PFOA, and it could be attributed to additional PFOA mass loading from the bottom 900 g layer of native site soil.



Once applying the AC layer beneath the high PFAS-containing soil, the cumulative leaching of PFOA, PFBS, and PFOS significantly reduced. Figure 2B The cumulative leaching of PFOA, PFBS, and PFOS from PAC-treated soil is 6.7%, 7.5%, and 3.1%, respectively, during the simulated 102-inch precipitation. When using micron-sized CAC (i.e., SourceStop), the leachability dropped more than 1 order of magnitude for PFOA, PFBS, and PFOS to 0.2%, 0.6%, and 0.05%, respectively. It suggests the rapid sorption process provided by CAC, which can be critical to retain leaching PFAS from the source during extreme rain events.

Both AC adsorbents show similar sorption affinity to different PFAS compounds. For the three discussed compounds, the leaching percentage from high to low is PFBS, PFOA, and PFOS from both AC-treated cells. It suggests AC-based adsorbent tends to adsorb PFAS with longer fluorinated chain length (PFBS vs. PFOS) Footnote 1 and PFAS with sulfonic acid over with carboxylic acid (PFOA vs. PFOS). Footnote 2 Since some legacy AFFF is mainly composed by PFAS with sulfonic acids, especially PFOS, our results demonstrate using AC sorbents is a promising approach to remediate AFFF-impacted sites.

PFBS has 4 fluorinated carbons and PFOS has 8 fluorinated carbons

PFOA has carboxylic acid functional group and PFOS has sulfonic acid functional group

Figure 2A

PFOA PFBS

PFOS

Cumulative leaching percentages of PFOA,

PFBS, and PFOS as a function of cumulative

Cumulative Leaching Percentages of PFOA, PFBS, and PFOS



Figure 2B

- ····o··· PFOA-SourceStop - PFOA-PAC PFBS-SourceStop
- PFBS-PAC
- ····· PFOS-SourceStop
- PFOS-PAC



SECTION 4.2 Leachability Results for total PFAS

The cumulative total PFAS leaching percentage from AFFF-impacted soil throughout the experiment is illustrated in **Figure 3**. The total cumulative PFAS leached percentage from the control was 97.7%, resulting in very little PFAS retained on the native site soil during the simulated heavy/very heavy rain events.

Similar to what was observed for the three representative PFAS in Section 4.1, the applied AC layers blocked most leaching PFAS migrating into downgradient. After 102 inches of precipitation, total PFAS leaching was 0.3% from the SourceStop treated cell, while it was 3.6% with PAC applied layer. The one order of magnitude lower of total PFAS leachability from SourceStop treated soil emphasizes the advantage of CAC over PAC. Less than 1% total PFAS leaching demonstrates that SourceStop successfully retained almost all of the PFAS mass in the vadose zone during the simulated extreme rainfall.

As mentioned in Section 3.0, the effluent from SourceStop-treated cell turned black-ish to clear after 75-inch precipitation. Based on the measured carbon concentrations in the effluent, it implies that 86% of the sprayed CAC was retained in the vadose zone. No significant change on PFAS leaching from SourceStop-treated soil during 75 to 100 inches precipitation, suggesting that the retained CAC can keep adsorbing the leaching PFAS effectively.





SECTION 5.0 Summary & Conclusion

PFAS leaching from AFFF-impacted soil during heavy/very heavy rain events and the performance of AC layer beneath the source zone were evaluated. The role of carbon size on adsorbing leaching PFAS via the AC layer was tested by using PAC and CAC. Our 102-inch simulated precipitation experiments show:

- 1. The laboratory experiment indicates that untreated, naturally occurring soils encountered at most sites will readily leach PFAS when exposed to precipitation. Almost all spiked PFAS (97.7%) leached out in this rainfall experiment, including PFOA and PFBS.
- 2. Applying AC layer beneath the PFAS source zone significantly reduced PFAS migrating downgradient.
- 3. By reducing AC size more than 100 times, the micron-sized CAC provide stronger barrier to reduce PFAS leaching into downgradient. Given by CAC advantages, SourceStop rapidly sorbs PFAS and the total PFAS leaching was 0.3% after 102 inches heavy/very heavy rain events. This leaching through the vadose zone was one orders of magnitude lower compared to PAC.
- 4. For the three specially concerned PFAS compounds, sorption affinity provided by AC from high to low is PFOS, PFOA, and PFBS. This suggests that AC is a promising technology for AFFF cleanup works because PFOS can be the dominant PFAS in AFFF formula.
- 86% of sprayed CAC retained in the vadose zone under extreme precipitation conditions, and the retained carbon can keep adsorbing leaching PFAS. It indicates that the majority of applied SourceStop is able to build up a reliable horizontal barrier to prevent PFAS leaching into saturated zone.



This test shows how SourceStop can be effectively applied as a basal source zone treatment to minimize PFAS leaching from the soil, creating a powerful *in situ* horizontal barrier to protect underlying groundwater. Applying SourceStop beneath the AFFF-impacted source zone, the micron-sized carbon adsorbed PFAS rapidly, severely restricting their leaching to the simulated groundwater surface compared to the native

SourceStop applications will be completed with further PFAS immobilization or soil stabilization amendments above a SourceStop-treated layer. Additionally, in many cases, these source zone treatments will be incorporated with vertically emplaced PlumeStop permeable reactive barrier(s) downgradient of the source zone to prevent the horizontal migration of PFAS in groundwater. These remedies, in combination, provide unmatched protection against human and environmental exposure risks associated with PFAS source zones.

SECTION 6.0 References

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- US EPA O. SW-846 Test Method 1312: Synthetic Precipitation Leaching Procedure. Published December 8, 2015. Accessed April 15, 2022. <u>https://www.epa.gov/hw-sw846/sw-846-test-method-1312-synthetic-precipitation-leaching-procedure</u>
- 8 Basis of Regulations PFAS Per- and Polyfluoroalkyl Substances (itrcweb.org);

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