



PFAS REMEDIATION AND PLUMESTOP

Frequently Asked Questions (FAQs)

Introduction

Recently, Scott Wilson, President and CEO of REGENESIS, presented on the effectiveness of using PlumeStop to eliminate risk on sites where PFAS contaminants are found. The talk covered the science and technology behind PlumeStop as well as a case study where PlumeStop was effectively applied at a site where PFAS contaminants were present and continue to be at non-detect with over 22 months of monitoring data.



*Scott Wilson, President and CEO
REGENESIS*

The following Q&A is a result of the questions posed during Mr. Wilson's talk.

Q: Can other non-target compounds block available adsorption sites for PFOS?

A: Absolutely. This is exactly why we developed the competitive sorption model that I displayed. Any more hydrophobic contaminant or native organic material can and will compete for sorption sites on the PlumeStop particle. When we design PlumeStop applications we do our best to have the background geochemistry of the groundwater understood. Any known organics that could interfere are put into the model to view expected impact. Also we have a quick and dirty lab bench test to discern gross competitive sorption impacts using site water. Sort of a go no go test.

Q: Does the PlumeStop get spent over time and have to be replenished?

A: The PlumeStop never gets "spent" in the sense that it will remain as part of the aquifer and will continue to sorb contaminants. It will however potentially become "filled up" with PFAS if there is a continuous incoming flux. This is because PFAS compounds do not biodegrade like BTEX or chlorinated compounds. In which case biodegradation of sorbed compounds allow for sorption sites to be "opened up" for additional future sorption. If, in the case of PFAS, the existing PlumeStop becomes saturated with PFAS, you simply re-inject additional PlumeStop right over the older PlumeStop. We have seen no negative impacts upon hydraulic conductivity.

Q: What are the impacts to dissolved oxygen?

A: We have not observed any impact on oxygen with PlumeStop. If anything, there is a low-level increase post injection from the aerated water being injected if no measures were taken to remove DO in the tank. Any propensity for activated carbon to remove/react with oxygen is consumed in the manufacturing process.

Q: Is PlumeStop more effective for short or long chain PFCs?

A: The more hydrophobic the more sorptive the contaminant. So the least sorptive are the short chain PFAS such as perfluorobutanoic acid (PFBA). However, PlumeStop is very effective at treating PFBA-it's just a matter of how much PlumeStop and how long a PlumeStop treatment zone you create. Remember, unlike P&T systems employing GAC, *In Situ* treatment with PlumeStop has HUGE residence time (weeks, months or years!) where GAC canisters usually have around 10-15 minutes of residence time.

Q: If there's PFOS and PFOA impacts along with BTEX impacts, will BTEX impact compete/lessen the benefits of PlumeStop?

A: Yes, BTEX will compete with the PFOS and PFOA for the sorption sites on the PlumeStop. However over time the BTEX will biodegrade opening up those sorption sites for additional contaminant sorption. If you have co-mingled plume we would be happy to model the competitive sorption and estimate the longevity of a PlumeStop treatment for you.

Q: Does this work on 1,4-dioxane and if so up which concentrations has PlumeStop been demonstrated to be effective? On PFAS, which concentrations has this been shown effective? How effective could it treat a 10 mg/L PFOA plume?

A: Currently we do not recommend PlumeStop for treatment of 1,4-dioxane. On PFAS PlumeStop performs very well. The technology can treat a broad range of PFOA from very low concentrations to PPM levels. As discussed, remember that the higher the starting concentration the less effective any activated carbon in a relative sense. You are further up the isotherm curve. Having said that it is most likely cost effective relative to alternative such as pump & treat.

Q: We understand the retardation factor, but we aren't clear about what happens once the carbon surfaces are all taken with PFAS.

A: Sorption of any contaminant onto carbon is always a dynamic equilibrium. Nothing is ever sorbed and bound forever. That's why we refer to PFAS treatment with PlumeStop as a retardation. If PFAS continues to flux into the PlumeStop treated aquifer zone, then eventually all sorption sites will become full and PFAS will leak out the other side. But this will most likely take decades and decades! If you have a prospective project we would be happy to model the expected longevity of a PlumeStop application.

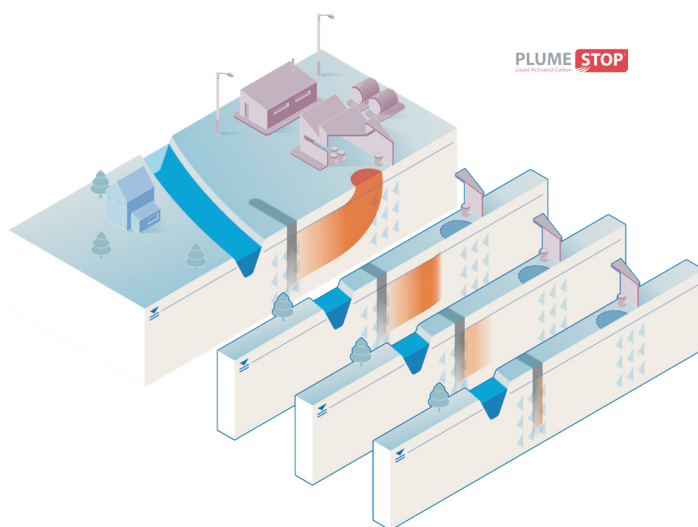
Q: Do you have any PlumeStop Performance data for the less adsorbing perfluoroalkyl acids (PFAA)?

A: Yes. We have data showing sorption of a range of PFAS constituents. During the webinar on eliminating risk from PFAS, I believe I showed data from an actual site lab evaluation. It is very important to understand (and few do) that the mix of PFAS species in a plume changes as the water moves forward into the PlumeStop

treated aquifer zone. As the plume moves forward it leaves behind a greater amount of the more hydrophobic PFAS species bound to the first encountered PlumeStop than of the less hydrophobic species. This continues as the water moves through the treatment zone effectively stratifying the species (just like in chromatography). Thus, if the design is correct the less hydrophobic species (e.g. PFBA) move the furthest and encounter virgin PlumeStop with little competition for sorption sites and are thus effectively removed from solution.

Q: How long will a PlumeStop barrier be effective? At what point might the barrier become saturated and allow some breakthrough?

A: The longevity of a PlumeStop barrier (a portion of the aquifer flux zone treated with PlumeStop) is determined by several factors. First is the characteristics of the contaminant plume (rate of contaminant flux, contaminant species present, other organics present that could competitively sorb, etc). Second is the installation design itself (amount of PlumeStop applied per unit volume of aquifer flux zone, the barrier thickness (the distance of PlumeStop treated aquifer that the plume will have to migrate through). Under most circumstances the estimated longevity of a PlumeStop barrier meeting regulatory objectives is on the order of many decades.



PlumeStop barrier example

Q: If you had a PFAS impacted drinking water well, could PlumeStop be applied to that well and area surrounding and make that well usable then for drinking water?

A: Really good question. We are in the throes of trying this now. We hope to be able to mobilize to an impacted domestic well, inject down the well and out into the formation, let it sit for a couple weeks then purge the well. Hypothetically this would result in a “doughnut” of PlumeStop around the well, protecting it from a myriad of contaminants including PFAS. At this point this is unproven...but in the works. Alternatively we could simply use a direct push or augur rig and inject PlumeStop around the water well.

Q: How do other contaminants (ex. hydrocarbons) affect the retardation of PlumeStop for PFAS?

A: Any more hydrophobic contaminant or native organic material can and will compete for sorption sites on the PlumeStop particle. When we design PlumeStop applications we do our best to have the background geochemistry of the groundwater understood. Any known organics that could interfere are put into the model to view expected impact. Also we have a quick and dirty lab bench test to discern gross competitive sorption impacts using site water. Sort of a go no go test.

Q: What was the totality of the PFASs monitored when evaluating the efficacy of PlumeStop? How would you project the effectiveness of PlumeStop to other, unmonitored PFASs?

A: If you absolutely want to know the totality of PFAS that PlumeStop treats, I think it would be best to first analyze the water via 537 without TOP analysis. Then measure with TOP analysis. The difference would be the precursors that didn't show up on the 537, but were oxidized so as to be seen in the TOP assay. Then subject a sample of the water to our quick and dirty batch sorption test and analyze by 537, that will show all that is sorbed in the natural state without oxidation. The quick and dirty test I refer to will underestimate the performance of the PlumeStop as in a batch test will all of the PFAS species there is competitive sorption which will result in more soluble species being outcompeted for binding sites. This is not what happens in the field as less soluble species are removed from solution first as the plume progresses through the PlumeStop treated zone leaving the more soluble species to move forward with less competition for sorption sites. So the further a plume "chromatographs" the more effective the PlumeStop becomes.

Q: Could you provide the citation of the research article that you mentioned during the webinar about eliminating risk from PFAS with colloidal activated carbon?

A: McGregor, R. *In Situ* treatment of PFAS-Impacted Groundwater Using Colloidal Activated Carbon. REMEDIATION, 2018; 28:33-41. Wiley. Here is a link to the paper: <https://regenesiS.com/en/download-the-research-article-in-situ-treatment-of-pfas-impacted-groundwater-using-colloidal-activated-carbon/>



Rick McGregor, President of INSITU Remediation Services, Ltd. and author of, "In Situ Treatment of PFAS-Impacted groundwater Using Colloidal Activated Carbon"

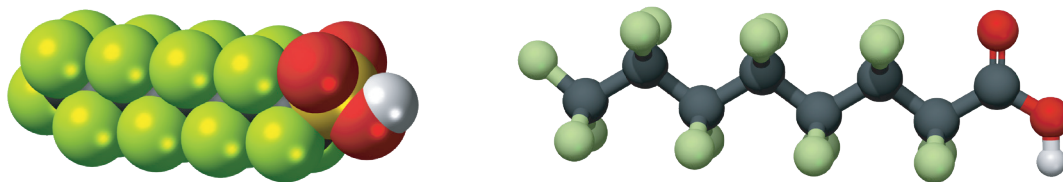
Regulatory Questions

Q: When an NFA is issued, are institutional or engineering controls typically implemented after the use of PlumeStop?

A: So far our discussions with regulatory agencies have all included the notion of having a sentinel well(s) downgradient of the PlumeStop barrier that is analyzed periodically (i.e. once a year) to ensure that the PlumeStop is working as designed. This is a form of institutional control that would go with the NFA.

Q: What are the regulatory standards today for PFOA? and PFOS? [Matthew Basso]

A: This is a complex question as there are no federal standards for PFAS, simply health advisory levels. Many states have promulgated their own standards. A good reference is the ITRC. Here is a link to their PFAS standards information: https://www.itrcweb.org/About/2018-Updated-Information-on-PFAS-standards-and_Guidance-Values



PFOA and PFOS are the two most commonly encountered examples of Per- and Polyfluoroalkyl Substances (PFAS). PFOA and PFOS are abbreviations for the chemicals “perfluorooctanoic acid” (PFOA) and “perfluorooctanesulfonic acid” (PFOS).

Q: What concerns do you see with EPA creating formal regulation of PFCs that would require concentration and/or destruction methods of treatment?

A: With PlumeStop, the waste is never “generated” in regulatory terms. Therefore the practitioner using PlumeStop does not have to worry about transport to a permitted Transportation, Storage, Disposal Facility (TSDF). Use of PlumeStop would be a most elegant, and cost effective solution under the scenario of EPA creating formal designation of PFAS as a hazardous material (waste).

PlumeStop Questions

Q: Is the colloid engineered for optimal pore size? Are other configurations useful for other contaminants?

A: Yes we have engineered the colloid for optimal distribution through the size we chose to mill it to (1-2µm) and through the dispersants and polymers we use to coat the particles with. This combination was optimized to induce flow through the pore throat diameters found in silts. We have developed different forms of colloidal carbon for different uses. For example we have a form of colloidal carbon that is higher in carbon concentration, but lacks

the distribution properties of PlumeStop...this is used on sites that have very high contaminant concentrations or where high groundwater flow velocities may “wash out” regular PlumeStop. We also are about to launch a form of colloidal carbon aimed specifically at the retail petroleum gas station market that includes electron acceptors so as to stimulate rapid hydrocarbon biodegradation.

Carbon Particle Sorption Comparison

Granular Activated Carbon (>500µm):

Slow sorption due to limited surface area exposed to solute



Colloidal Activated Carbon (1-2µm):

Rapid sorption and more complete use of sorption sites



An illustration of the importance of particle size. If a pound of carbon is 500 microns in size, it will sorb the PFAS represented by the red outline around the surface area of the particle. Conversely, that same amount of carbon, ground it up into colloidal activated carbon that is 1 to 2 microns in size, will make all the absorption sites on the 1 to 2 micron-sized particles available to PFAS. The smaller the size, the faster the PFAS contaminants reach all the absorption sites.

Q: How much is the SSA (Specific Surface Area) of PlumeStop colloidal activated carbon?

A: We are currently using as raw material typical water treatment activated carbon (virgin). The iodine number of these carbons are in the range of 1000 (minimum).

Q: I'm curious if the polymer coating which prevents the carbon from coagulating has any negative impact on the sorption of the carbon

A: The polymer that is wrapped around the particle we think helps to establish the attachment of the particle to the aquifer surface. In our early laboratory work we showed that the presence of the polymer did not affect the particle uptake of PFAS. More recently, however it appears that the polymer may negatively affect the carbon particle uptake of the contaminant if the contaminant is present in very low concentrations. Keep in mind that once the particle is attached to the aquifer matrix the polymer degrades leaving the naked carbon particle bound to the aquifer. At that point (perhaps a month after application) there is no longer any negative effect of the polymer and we see full sorption of the low concentrations of contaminants.

Q: Most mineral surfaces in soils, organic matter and in aquifer pore spaces are already negatively charged, so please explain how your negatively charged PlumeStop colloidal activated carbon will sorb to surfaces in an aquifer???

A: We know the polymer we use presents negative charges and we know from extensive empirical evidence that the polymer-wrapped particles stick upon initial contact with aquifer material, and do not wash off even after the polymer is long gone. Also, we know that adding increasing amounts of clays (with negative surface charges) increases PlumeStop particles sticking to the aquifer matrix in column studies. Our speculation is that the polymer, which is wrapped around the carbon particle and presents negative charges is strongly influenced by the zeta potential of the aquifer materials. So the hypothesis goes something like this:

Upon collision with the aquifer matrix most negatively charged colloids attach rapidly to the matrix surface through physical forces. The forces binding the attachment are the balance of electrostatic repulsion and van der Waals attraction that occurs within the surface potential of the ionic environment in what is referred to as the "double layer" and is explained by DLVO theory (named after Derjaguin, Landau, Verway, Overbeek).

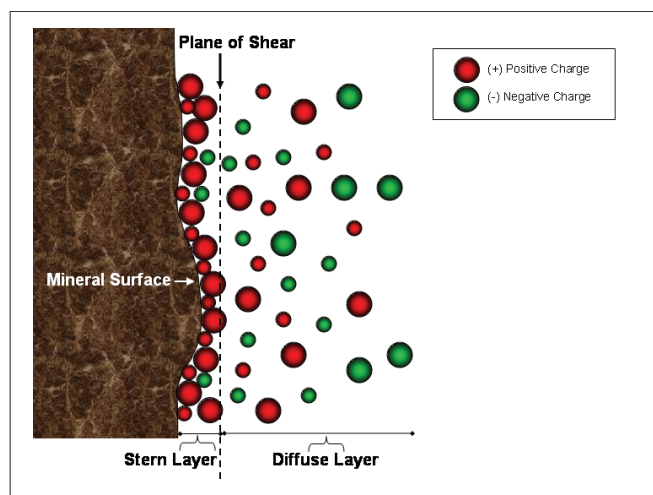


Figure 1: Ionic Environment on Surface of Aquifer Matrix

This phenomenon is often simply referred to as “colloidal adhesion” due to zeta potential, where zeta potential describes the electrokinetic potential at a point near the surface of a particle, defined as the slip plane or shear plane where surface charges begin to be diffuse and are subject to movement and colloidal attachment. Figure 1 illustrates the typical ionic environment on the surface of an aquifer matrix (Mysels, C. 1964. Introduction to Colloid Chemistry. Interscience.pp.332-356. New York, NY.)

As a colloidal particle such as a PlumeStop particle, wrapped in negative charges contacts the mineral surface, it enters through the diffuse layer, binding to the strongly attached ionic layer referred to as the Stern Layer.

As far as understanding the firm attachment that occurs after the polymer is gone (washed away or biodegraded) we assume this is due to a combination of any remaining surface charge interaction and Van der Waals forces.

Q: What is the fate of the polymer coating over time?

A: Over time (about one month) the polymer generally appears to biodegrade away or is washed away. The carbon particle however remains tightly bound to the aquifer matrix, presumably due to remaining charge attraction between the carbon and aquifer matrix and due to Van der Waals forces. We have undertaken considerable effort in laboratory studies to wash off the remaining carbon layer in column studies with no success. The stuff is stuck permanently.

Q: Has PlumeStop been used in a permeable reactive barrier and can a case study using monitoring wells (gravity fed) be provided?

A: Use within a permeable reactive barrier:
Yes. The large EPA Superfund project was to retrofit an existing trench system. The site has a downgradient sheet-pile retaining wall. Upgradient of the wall and down-gradient of the wall are trenches that connect through ports in the sheet-pile (to relieve the water building up). PlumeStop was flooding in all of the trenches to convert the trench gravels into a PlumeStop filter to sorb PFAS. So we actually retrofitted the trench system.

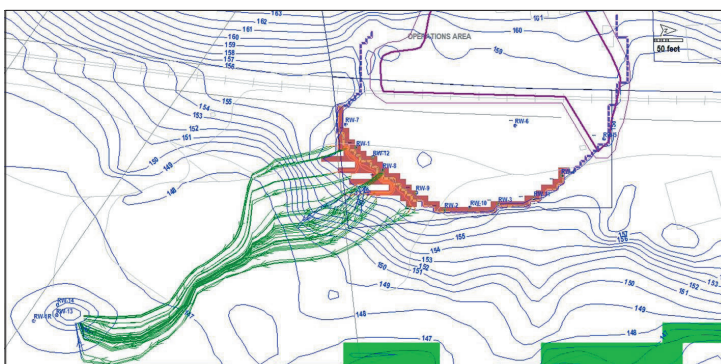


Figure illustrating predictive groundwater flow model output with sheet pile wall (purple), trench system (red) and groundwater flow lines (green)

We have not used PlumeStop in monitoring wells as it just does not seem right to inject in true monitoring wells if you plan to monitor from them again. However, if you can convert a monitoring well into an injection well, then there is no reason it should not work! Depending upon how much time you have, you can gravity PlumeStop into wells or perform low pressure injection. Either way.

Q: You recommend injecting PlumeStop at lower injection pressures than other in-situ substrates or applying PlumeStop via gravity or natural aquifer flow?

A: Yes. Currently there is a group selling powdered activated carbon that has to be “fracked” into the subsurface under high pressure. PlumeStop is nothing like this. PlumeStop can be poured into application wells where it will gravity feed into the flux zone. I am an advocate of this approach, but it may take some time. Usually it is applied under low pressure into the aquifer (say <20 psi).

Q: How well will the colloidal activated carbon (PlumeStop) work to control back diffusion in fractured bedrock? Related question - Is the particle size small enough to penetrate the crystalline matrix of rock?

A: I think it should work really well in most fractured rock settings to stop matrix back diffusion IF enough PlumeStop will stick to the fractures. To that end we have a different formulation of PlumeStop for high flow settings and large fracture settings. The formulation is higher in carbon concentration and lower in dispersion chemistry- thus more apt to coat the fracture surfaces to catch the back-diffusion from the matrix. As far as penetrating crystalline rock... I don't think the particle is small enough. But if it coats the surface the PlumeStop should soak up the contaminants before they enter the flux zone.

Q: How does PlumeStop work with NAPL?

A: It does not work with NAPL. NAPL is simply too concentrated and would require too much PlumeStop. I would recommend physical removal followed by chemical oxidation then perhaps some form of PlumeStop/ bioremediation.

Q: How do you monitor the quality/density/uniformity of the original placement of the PlumeStop ?

A: Really good question. If you have wells in the area you can look for black water entering the wells thus indicating that the flux zone intersected by that well is impacted by the PlumeStop.

Additionally you can sample soils post- PlumeStop injection and sample for the presence of elevated carbon concentrations (indicating bound PlumeStop). Below is an excerpt from a REGENESIS Research and Development memo outlining Total Organic Carbon analyses appropriate for evaluating the presence of PlumeStop.

A major feature in PlumeStop is its ability to distribute widely in the subsurface. This provides the client with an effective way to treat migrating contaminant plumes. A key metric in determining success is to study the treated area and assess if the applied material reached its intended area.

Total organic carbon or TOC measurements are a common parameter used in the analytical toolbox for groundwater remediation. There are several other names for this method, including EPA 415.1 SM5310B or EPA9060A for analysis of soil and groundwater. There are several types of organic carbon measurements. The two most common are combustion and wet oxidation. Due to the difficulty of oxidizing elemental carbon, wet oxidation with persulfate cannot accurately quantify the carbon present from PlumeStop additives and the activated carbon itself. Therefore, it is crucial that any TOC measurement done uses the solid combustion method.

R&D recommends using this method, which is commercially available at several labs across the country that can give semi-quantitative results for PlumeStop determination.

Analytical Lab	SOP / Analysis ID	Locations	Cost
Test America	EPA 9060A/SM5310B	St. Louis, MO Pittsburgh, PA Canton, OH Denver, CO Edison, NJ Buffalo, NY Nashville, TN Chicago, IL Seattle, WA	\$60.00
ALS Global	EPA SW9060	Tuscon, AZ	\$60.00
Eurofins Calscience	SM5310B	Garden Grove, CA	\$80.00
Pace Analytical	EPA 9060A	Virginia, MN	\$45.00
Weck Laboratories	EPA 9060M	City of Industry, CA	\$95.00

A: Key analysis parameters to determine with your analytical lab include the use of a solid state module or equivalent that can process solid samples instead of aqueous slurry suspensions and that the combustion chamber reaches at least 900°C during the sample analysis. It is also crucial that all analytical samples for TOC do not contain any preservative. The standard acidic preservative, can destabilize the colloid, providing inaccurate quantitative results. R&D can provide laboratory recommendations and assistance in finding and vetting qualified labs for TOC testing.

Lastly, we are currently considering the development of protocols using dual tracer dyes that could establish the background retardation in the aquifer, then the elevated retardation in the presence of the PlumeStop treated zone. This is a bit tricky and we are currently looking for sites to calibrate the process on. Stay tuned!



Q: In a more mature release scenario where the majority of mass flux is from a slow advective zone into a higher permeability transport zone, how do you get Plumestop distribution into that lower permeability zone without pressure injection methods?

A: You probably want to inject into the slow advective zone where you have the majority of the flux. You can inject under any pressure you like. We generally use low pressure (say <20psi). The trick is to find the zone vertically and flood it. If you are referring to a back-diffusion situation you might want to simply flood the high permeability zone. In doing so you will be coating the contact between the low and high perm zones as well as the high perm aquifer material-thus very likely to sorb all of the back diffusion contaminants before they move very far.

Q: Have you used colloidal activated carbon (PlumeStop) in ex-situ applications for above grade treatment?

A: I believe it has been used (sprayed) into open excavations to bind up contaminants below the excavation.



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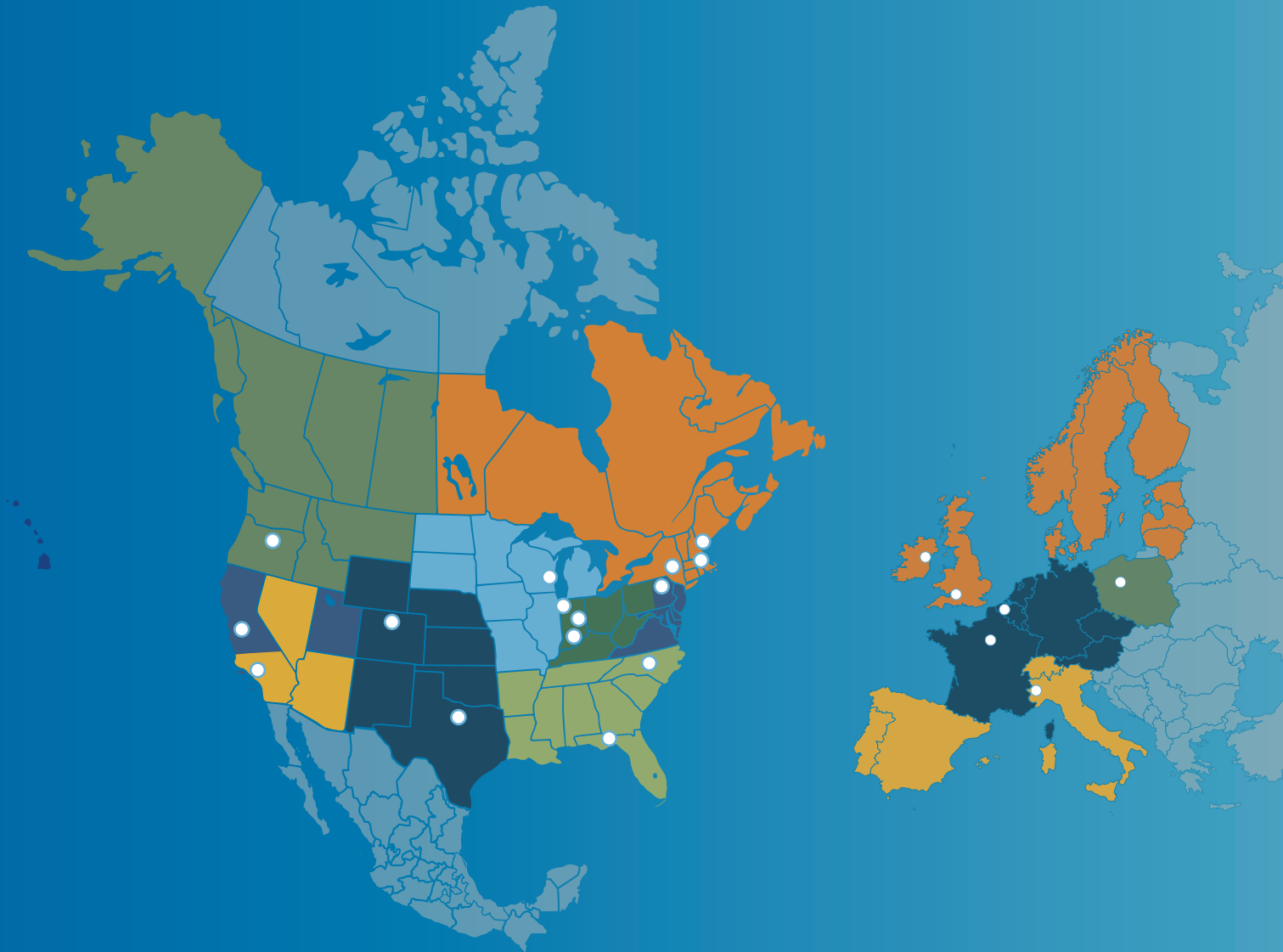
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Global Headquarters

San Clemente, CA 92673 USA
Ph: +1 949 366-8000

Europe

europe@regenesiS.com



www.REGENESIS.com

1011 Calle Sombra, San Clemente, CA 92673

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