

White Paper: Surfactant-Enhanced In Situ Chemical Oxidation (S-ISCO®) Technology

1.0 Background

EthicalChem's patented Surfactant-enhanced In Situ Chemical Oxidation (S-ISCO®) was developed to treat tightly sorbed, hydrophobic contamination and residual Non-Aqueous Phase Liquid (NAPL) contamination in soil. Free phase and soil sorbed contaminants are often a source of groundwater contamination, slowly leaching into the water over time. Technologies designed to treat groundwater, such as In Situ Chemical Oxidation (ISCO), do not adequately address this separate contaminant phase, providing only a temporary solution for previously dissolved contaminants in groundwater. Through time the untreated NAPL source leaches back into the groundwater, re-establishing the contaminant equilibrium, in a process known as rebound. By targeting the residual NAPL and soil contamination with S-ISCO, the contaminant source is addressed, thereby eliminating rebound and providing permanent solutions.

The S-ISCO process utilizes EthicalChem's proprietary, plant-based, biodegradable surfactant and co-solvent blends which are specially formulated to co-exist with oxidants while desorbing and emulsifying contaminants that are immiscible with water, such as heavy hydrocarbons and residual NAPLs. During the S-ISCO process, surfactants and oxidants are injected simultaneously to destroy contamination on-site and in-place, providing timely and permanent solutions to soil, water, and residual free-phase contamination. In cases where there is significant NAPL in the subsurface, EthicalChem first implements Surfactant Enhanced Product Recovery (SEPR), a patented process which utilizes higher surfactant concentrations along with low doses of hydrogen peroxide to remove free phase product through recovery wells. Following the removal of bulk NAPL, S-ISCO is implemented to treat the remaining contamination in place.

S-ISCO has been applied at over 100 sites in thirteen countries, including three US EPA Superfund sites. S-ISCO and SEPR have remediated Light and Dense Non Aqueous Phase Liquids (LNAPLs and DNAPLs), and sorbed residuals associated with various industrial and residential sites such as former Manufactured Gas Plants (MGP), sites contaminated with coal tar, creosote, home heating oil, fuel oils, and dry cleaning operations.

2.0 Technology

NAPL contamination is present at more than 200,000 waste sites in the United States alone. At sites where NAPL was released to the subsurface many decades years ago, significant residual quantities still remain. S-ISCO was specifically developed to target this free phase material, which is highly hydrophobic. The hydrophobic nature of these contaminants makes it extremely difficult to address with technologies aimed at only groundwater treatment.

2.1 In situ Chemical Oxidation (ISCO)

ISCO consists of aqueous phase reactions that take place in the groundwater. The highly hydrophobic contaminants are sorbed to soil particles and may also exist in a separate NAPL phase with limited partitioning into the groundwater phase. As a result of their very low solubility in water, these sorbed and non-aqueous phase contaminants are not available for reaction with an injected oxidant which resides in the aqueous phase.

Although ISCO treatments may deliver short-term decreases in groundwater contamination, these decreases are the result of oxidizing the already dissolved impacts. Since this technology fails to address the source of

contamination, contaminant rebound is expected, as the sorbed and free phase material re-establishes solubility equilibrium and dissolves into the aqueous phase. This is illustrated in **Figure 1** which shows the decrease and subsequent return (rebound) of groundwater tetrachloroethylene (PCE) contamination following an ISCO treatment. As illustrated, the ISCO treatment reduced groundwater levels to below remedial goals, however, groundwater concentrations soon re-elevated due to rebound of the PCE leaching back into the groundwater from the unaddressed soil and free phase plume. This would result in additional ISCO treatments.

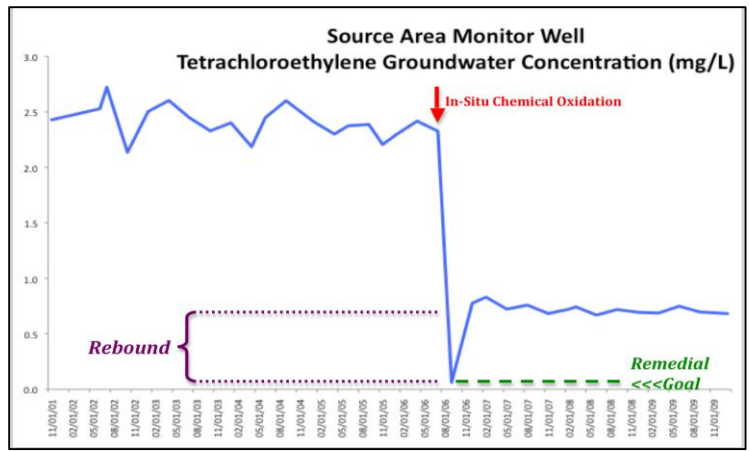


Figure 1. Groundwater PCE (ug/L) in Source Area, Relative to ISCO

2.2 Surfactant-enhanced In Situ Chemical Oxidation (S-ISCO)

The foundation of EthicalChem’s S-ISCO technology is combined transport of surfactants and free radical oxidant systems to achieve the three key attributes of S-ISCO:

- Emulsification/solubilization of NAPL and desorption of contaminants from soil by injection of surfactant/co-solvent mixtures
- Oxidation of solubilized contaminants by free radicals
- More efficient use of oxidant through increased contact between free radicals and contaminants

The S-ISCO process increases the solubility of contaminants, such as petroleum hydrocarbons, that are immiscible with water and pulls sorbed contaminants from the soil, making them available for simultaneous oxidative destruction. By addressing the source of contamination, EthicalChem’s remedies reduce the *source* of contamination thereby achieving complete or near complete contamination removal, eliminating rebound and the need for follow-up treatments.

2.2.1 E-Mulse

S-ISCO uses E-Mulse (plant-based, biodegradable surfactant/co-solvent mixtures) to address tightly sorbed and NAPL-phase contamination. Surfactants are amphiphilic molecules possessing both hydrophilic (water-loving) heads and lipophilic (fat- or oil-loving) tails. When the E-Mulse surfactants enter the subsurface the lipophilic tail is attracted to NAPL while the hydrophilic heads are attracted to the aqueous phase. This creates micelles, aggregates of surfactant molecules encasing the NAPL and bringing it into the aqueous solution (**Figure 2**).

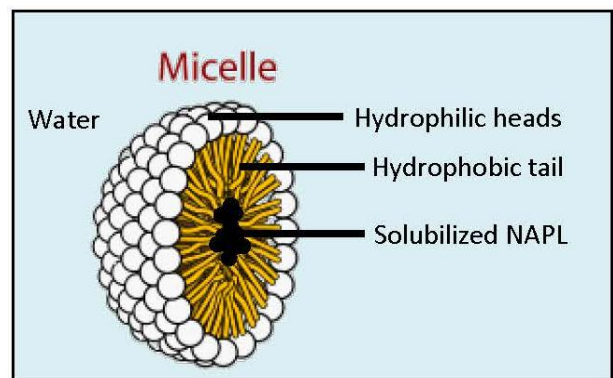
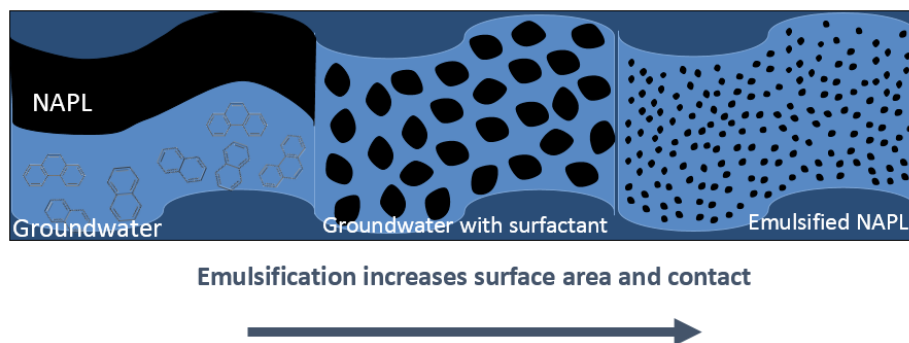


Figure 2. Surfactant micelle with solubilized NAPL

The formation of a micro-emulsion increases the amount of NAPL present in the aqueous phase, thereby increasing the surface area of NAPL exposed to the oxidant solution (**Figure 3**). This increase in surface area drastically improves the exposure of NAPL to the aqueous phase oxidation reactions.

Figure 3. Surfactant effect on NAPL when emulsified



Because the partitioning rate of contaminants into the aqueous phase affects the overall rate of reaction, as E-Mulse causes the concentration of contaminants in the aqueous phase to increase, the efficacy of chemical oxidation is increased. Therefore, using E-Mulse increases the rate of soil decontamination by optimizing the oxidation of the NAPL.

2.2.2 Oxidant Selection

The free-radical based chemical oxidation systems used during S-ISCO can include activated sodium persulfate, hydrogen peroxide or sodium permanganate. The optimal oxidant and activator selection depends on the specific conditions of the site, including its contamination, hydrological and geological characteristics, and nearby sensitive receptors. EthicalChem can conduct laboratory tests using site soil and groundwater and/or pilot-scale field studies as part of the S-ISCO design process in order to optimize the chemical and implementation details. For large sites, pilot tests are also very informative for optimizing injection rates and concentrations, and determining flow patterns.

Oxidant and surfactant selection begins with an analysis of the site conditions, including:

- Contaminant type
- Contaminant concentration
- Contaminant phase—dissolved, sorbed to soil, and/or free-product
- Soil lithology

The chemical, hydrological, and geological conditions of the site are also considered, including groundwater depth and flow, water quality parameters such as pH, ORP¹, dissolved oxygen, and conductivity, and sensitive receptors or subsurface infrastructure in the vicinity of the treatment area.

Sodium Persulfate

Persulfate is used to treat more chemically complex contaminants, often in silty clay or bedrock environments. The persulfate ion ($S_2O_8^{2-}$) can react directly or be activated to form sulfate radicals ($SO_4^{\bullet-}$). Sulfate radicals are stronger oxidizing species with a redox potential of approximately 2.6 V (compared to 2.1 V for the persulfate ion and 1.8 V for hydrogen peroxide). The stability of persulfate, which can last weeks to months in the soil, provides a large radius of influence achieved by injections, and maximizes contact time with contaminants. As an example, following S-ISCO implementation at a New York MGP site, the results of continued groundwater monitoring showed that

¹ Oxidation-Reduction Potential.

persulfate remained active for more than four months after injections ceased.²

Another factor that increases the effectiveness of persulfate in treating chlorinated compounds, in particular, is that after oxidative reactions have ceased, a reducing environment can be created by fostering sulfate-reducing bacteria that will continue to degrade contaminants. In addition, because the subsurface transport of sodium persulfate is primarily density-driven, its injected concentration can be readily altered to increase or decrease its vertical transport. Density-driven transport along with a longer lifetime in the subsurface makes persulfate the optimal treatment for sites with deep or bedrock contamination. Finally, persulfate is often preferred for treatments beneath buildings or other areas in which there are concerns about the generation of soil vapors since, unlike peroxide, it does not generate a significant gas phase upon decomposition.

Hydrogen Peroxide

Hydrogen peroxide is an effective remedy for low to medium concentrations of less complex hydrocarbon contaminants, such as fuel oils and benzene, toluene, ethylbenzene and xylene (BTEX) in groundwater or unsaturated soils. When activated, hydrogen peroxide (H₂O₂) produces hydroxyl radicals (OH·) which rapidly react with and destroy aqueous phase contaminants.

Oxygen gas is produced as a byproduct of the decomposition of hydrogen peroxide. The oxygen gas enhances treatment of shallower depths, especially in the presence of a surfactant in which case the gas formation results in slight foaming of the surfactant which allows the treatment to reach above the water table.

Hydrogen peroxide decomposes quickly and completely into oxygen gas and water, and does not yield byproducts that may affect water supplies. Although its rapid decomposition in some soil matrices limits its transport and effectiveness, its short persistence and high reactivity are desirable in treatments where containing a very small radius of influence is valued, such as near sensitive receptors. When S-ISCO is implemented to treat contamination in the vicinity of metal-encased subsurface services, peroxide is the optimal oxidant since it will react very quickly and is not corrosive to metals, as could be the case with sodium persulfate.

Sequential Oxidant Treatment

As an alternative to separate persulfate or peroxide treatments, a two-phased remedy consisting of a preliminary hydrogen peroxide stage followed by a “polishing” sodium persulfate stage, may be used. These two-phased implementations are most effective for sites with high concentrations of BTEX or fuel oil contamination in sandy and/or gravelly soil matrices. The peroxide treatment phase will target shallower contamination and provide faster destruction of the more accessible contaminants. The subsequent persulfate phase will target the deeper, more tightly sorbed impacts and sustain a longer lasting oxidative treatment environment.

2.2.3 Activators

S-ISCO treatments can incorporate any of a range of activators to drive free-radical formation, and consequently increase oxidative strength. Activators used in S-ISCO treatments include:

- Sodium hydroxide
- Chelated iron, such as Fe-EDTA
- Green-synthesized Nano-iron Activator (GnA)

Alkaline Activation

Sodium hydroxide is frequently used for alkaline activation of sodium persulfate to generate free radicals. Typically sodium hydroxide is injected at a concentration that elevates and maintains subsurface conditions within pH 10 to 12. During field implementation, sodium hydroxide is adequately dosed to ensure proper activation of the

² Measured concentrations of persulfate as well as elevations in conductivity indicated its lasting presence and activity in the subsurface.

persulfate.

Iron Chelates

Chelated iron compounds, such as Fe-EDTA, are inexpensive and easy to use with both peroxide and persulfate. These activators function optimally at pH 4, which is a pH environment that the injected oxidants typically create and therefore does not require pH adjustments. During S-ISCO injections, the chelated iron activators are injected at concentrations up to 250 mg/L (as Fe).

Green-synthesized Nano-iron Activator (GnA)

GnA is an EthicalChem patented, highly effective activator, developed in collaboration with US EPA using green synthesis methods and plant materials. GnA can enable oxidants to destroy contaminants five times faster than Fe-EDTA or Fe-EDDS, at one-fourth of the concentration. Therefore, more oxidant is rapidly converted into free radicals and made available to destroy organic contamination, and less oxidant is scavenged by surrounding material such as minerals and metals in the soil.

2.3 Surfactant Enhanced Bioremediation

E-Mulse surfactants may also be used to enhance bioremediation at applicable sites. Desorption and emulsification of contaminants from soil into the aqueous phase enhance contact between contaminant and microbes. Surfactants can be combined with nutrients prior to injection, and simultaneously injected into the subsurface.

2.4 Pre-Treatment Product Recovery Phase

When significant NAPL and/or free product contamination is present, a product recovery phase may be implemented prior to S-ISCO or bioremediation in order to increase the efficiency and effectiveness of the in situ treatment. EthicalChem's patented Surfactant Enhanced Product Recovery (SEPR™) process utilizes surfactants together with very low concentrations of hydrogen peroxide to help loosen and facilitate movement of the NAPL toward recovery wells. Activators are not injected during the SEPR process, as the natural minerals and inorganic compounds present in the subsurface provide enough activation to breakdown the peroxide into oxygen gas and water. The SEPR process benefits from the formation of oxygen gas bubbles which act as a physical aid in desorbing and freeing the bulk free phase material from the soil. Implementation of S-ISCO or bioremediation after product recovery destroys residual contamination and polishes the soil. These sequential approaches provide a much faster and more cost effective solution for addressing bulk free phase contamination, rather than attempting to remediate by direct oxidation only.

3.0 S-ISCO Implementation

S-ISCO is typically implemented with an injection system that carries individual chemical streams through a metering pump and in-line mixers, where the chemicals are mixed together with water to appropriate concentrations before flowing to injection wells in the treatment area.

During site mobilization the injection and monitoring wells are strategically installed within and around the treatment area. Injection wells are spaced to ensure coverage of the entire contaminated area and screened to target the contaminated depths. Well placement and spacing vary based on site characteristics such as soil permeability, hydraulic conductivity, and contaminant distribution. When persulfate is used, wells may be screened above or across the upper extent of the contaminated interval since the injection solutions density will drive its vertical transport. Peroxide injection wells are typically screened within or below the contaminated interval since the oxygen production along with the surfactant will result in a rise upward. S-ISCO injections typically move with the local groundwater flow, however, in soils with low permeability additional technologies may be used such as pressure-pulsing and/or direct-push injections, emplaced fracturing and soil mixing.

Monitoring wells are used to track the movement of the injected chemistry through the subsurface, the progression of the oxidation reactions, and to evaluate and control potential travel of the chemistry toward sensitive receptors. A typical S-ISCO monitoring plan consists of:

- Tracking groundwater quality parameters, including ORP, pH, conductivity, temperature, and dissolved oxygen
- Measuring S-ISCO performance indicators, including interfacial tension (an indication of the presence of E-Mulse surfactants); oxidant concentrations, conductivity and ORP (indications of oxidants); and pH (indication of persulfate activation)
- Measuring groundwater contaminant concentrations, to confirm the effectiveness of treatment

Monitoring may also involve soil vapor monitoring and interim soil sampling for contaminant analysis.

3.1 Implementation Considerations

Several factors enhance the performance of S-ISCO in the field. The correct surfactant, oxidant, and activator are needed, at the correct dosage and formulation. The S-ISCO chemicals will be recommended based on site information. Additionally, a laboratory and/or pilot-scale test can be conducted to select optimal surfactants, evaluate the treatment effectiveness, optimize dosing parameters, and make any adjustments to the overall treatment plan. This is particularly true if a site has not been fully delineated and characterized, and the identity, composition, magnitude and distribution of impacts are incomplete.

Achieving maximum contact between the oxidant and contamination is imperative. The combined surfactant oxidant mixture must be transported efficiently and simultaneously through the subsurface to reach its target. This can be accomplished by strategic well spacing and screening, modifying the injection concentrations, and/or using peroxide, especially when preferential pathways may be present in the soil. Soils may be tight, clayey, unsaturated, and/or un-identified intervals of contamination may be found above or below the target interval. Emplaced fracturing, direct-push injection, and/or pressure-pulsing can be used to enhance injection spread and uniformity.

3.2 S-ISCO Applications

The following are examples of sites at which S-ISCO is applicable:

- Former Manufactured Gas Plant (MGP) sites
- Underground storage tank (UST) sites
- Superfund Sites
- Property Redevelopment & Brownfields
- Municipal Settings: Under schools, hospitals, buildings, and parking lots
- Pipelines: In place, under and between piping
- Railroads: Under and between railways and process equipment
- Industrial Settings: In fleet maintenance bays, parts-cleaning sumps, floors, equipment foundations and structures, pump stations, etc.
- Residential: Home heating oil tank spills and leaks, contaminated concrete basements, groundwater and yards
- Commercial: Manufacturers, dry cleaners, gas stations, etc.

Contaminants treated by S-ISCO include:

- Chlorinated compounds, chloroethanes, and chloroethenes
- Volatile organic compounds (VOCs), including BTEX
- Semi-volatile Organic Compounds (SVOCs), including PAHs
- DNAPL and LNAPL
- Petroleum hydrocarbons, including petroleum distillates, hydraulic fluid, and fuel oil No.2 and No.6

4.0 S-ISCO Case Studies

S-ISCO and SEPR technologies have been successfully implemented at over 100 sites throughout the United States and internationally for remediation of sites containing MGP residuals, coal tar, creosote, hydraulic fluid, home heating oil, and chlorinated solvents.

4.1 Field Implementation Summaries

The following sections summarize successful S-ISCO treatments. For additional full-length case studies please visit www.ethicalchem.com



NYSDEC issued a Certificate of Completion after successful cleanup of this Brownfield site in Queens, NY

Coal Tar Contamination, Former Roofing Manufacturer in Queens, NY

S-ISCO was implemented with alkaline activated persulfate during a five month treatment period to destroy coal tar related NAPL contamination located in the soil & groundwater at an urban Brownfield site in Queens NY. The primary contaminants of concern (COCs) included VOCs (BTEX) & SVOCs (PAHs and naphthalene) related to MGP coal tar used as part of the roofing manufacturing process.

S-ISCO destroyed >90% of total targeted contamination, including 95% of naphthalene. Off-site monitoring wells showed no transport of dissolved contamination or NAPL during or after implementation.

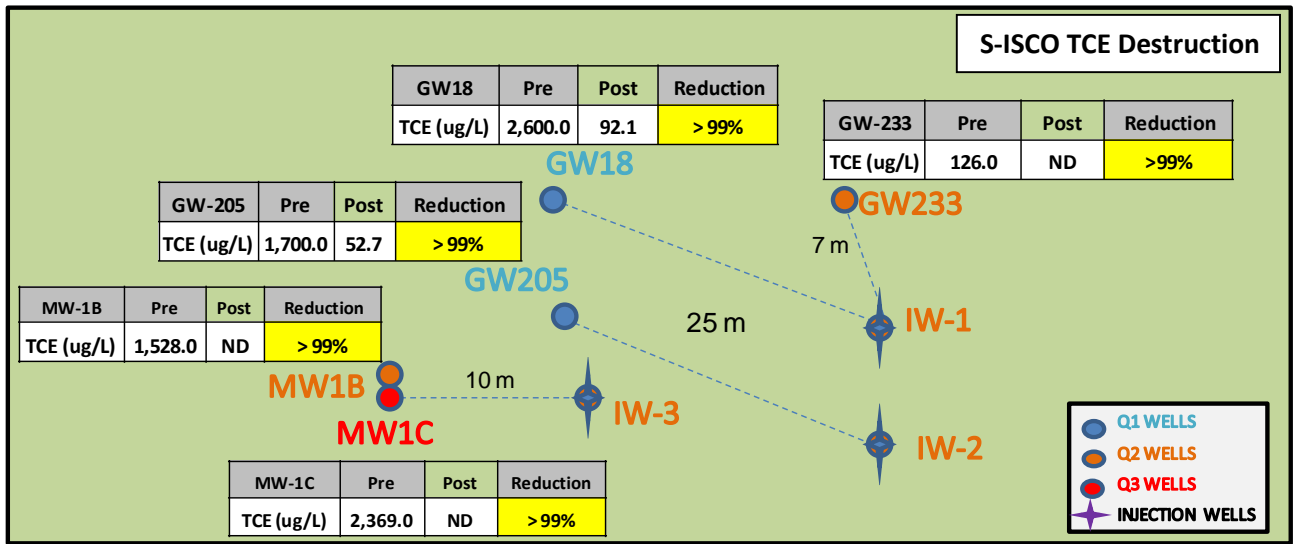
Soil vapor concentrations were significantly reduced including 100% benzene and naphthalene, and 98% BTEX.

S-ISCO implementation was completed without impacting the adjacent body of water (the East River) or the local community. The Certificate of Completion from NYSDEC was received in November of 2011, allowing the site to be redeveloped into a public library and park ranger station.

TCE Contaminated Department of Defense Site in Adelaide Australia

In 2011 a single S-ISCO treatment was implemented at a former Department of Defense site in Australia which was granted site closure in 2012. The treatment consisted of E-Mulse and alkaline-activated sodium persulfate applied at concentrations averaging 185 g/L persulfate, 7.7 g/L E-Mulse and 22 g/L sodium hydroxide.

The figure below shows the injection and monitoring well layout designed to evaluate the treatment efficacy and radius of influence. A comparison of samples collected from these wells before and after treatment showed greater than 99% reductions in TCE concentrations in a treatment zone measuring approximately 15 x 40 meters. This included non-detections at three wells (GW233, MW1B, and MW1C) and concentrations less than 100 ug/L at two wells (GW18 and GW205).



No. 2 Heating Oil Plume, Private Residence in New Jersey

S-ISCO was used to successfully remediate a DNAPL heating oil plume located in both the saturated and unsaturated soil zones at an inhabited residence in New Jersey. The S-ISCO treatment safely and effectively remediated the plume and reduced TPH contamination levels in both soil zones below state DEP criteria. Treatment consisted of two days of injecting a solution comprised of E-Mulse and hydrogen peroxide.

The S-ISCO treatment successfully reduced the average TPH (GRO) concentration in soil by 85%, from 13,625 mg/kg to 1,976 mg/kg. Post-S-ISCO TPH concentrations were not only significantly reduced but were also well below relevant clean-up criteria (4,000 ppm), as shown in **Figure 12**.

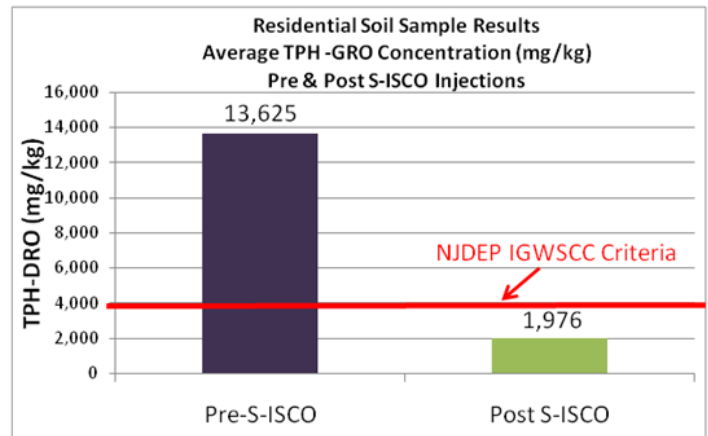


Figure 12 - Average TPH (GRO) Concentration

Petroleum Hydrocarbons, Gas Station in Connecticut

The technologies deployed at this complex site included Surfactant Enhanced Bioremediation as well as SEPR (Surfactant Enhanced Product Recovery) and S-ISCO (Surfactant-enhanced In-Situ Chemical Oxidation) at an active gas station in Connecticut to address TPH and NAPL contamination.

The SEPR phase of treatment included injections of low concentrations of hydrogen peroxide with EthicalChem proprietary surfactant E-Mulse 3 to facilitate NAPL removal via vacuum truck extraction. The SEPR phase was followed by the injections of alkaline activated sodium persulfate for S-ISCO treatment of the residual contaminants.

Within the service station dispenser islands a combined application of E-Mulse 3 surfactant and EthicalChem ECN-17 nutrients was implemented to enable bioremediation of petroleum hydrocarbons. Surfactants desorbed and emulsified the hydrophobic contamination from soil into the aqueous phase, enhancing the bioavailability of the contaminants, while the nutrients facilitate the stimulation and proliferation of the indigenous micro-organisms.

5.0 Environmental Benefits of S-ISCO

The S-ISCO technology was developed to provide an effective, efficient, and environmentally friendly solution to contamination that threatens human and environmental health and well-being. With its basis in Green Chemistry, S-ISCO delivers the Principles for Greener Cleanups published by the US EPA's Office of Solid Waste and Emergency Response (OSWER). These principles, printed in **Attachment 1**, guide the development and evaluation of remedial technologies based on energy use, air pollution and greenhouse gas (GHG) emissions, water resources, waste material, and land and ecosystems. The following details the performance of S-ISCO against each consideration.

- *Minimize Energy Use:* S-ISCO technology enables greater efficiency of the conventional ISCO processes by minimizing the project's duration and therefore the accompanying use of (energy-consuming) equipment. Additionally, S-ISCO addresses the source of contamination thereby eliminating rebound and the need for re-mobilization to the site and re-treatments. S-ISCO chemistry travels through the subsurface with the flow of groundwater, removing or limiting the need for re-circulating or extraction pumps. In addition, in situ remediation does not require the heavy machinery used in excavations to remove soil, reinforce excavations, and haul material off-site.
- *Minimize Air pollution:* Contaminated material is treated on site, removing the need for hauling it to landfills or disposal facilities with polluting vehicles. In addition, in situ treatment does not result expose contaminants to the air (as is the case in excavation), thereby reducing release of harmful volatile vapors. The use of surfactant and the formation of emulsions also inhibit the volatilization of compounds by emulsifying them (holding them) in the aqueous phase until destruction.
- *Minimize Impacts to Water Resources:* S-ISCO destroys the source of groundwater impacts. Additionally, during S-ISCO implementation comprehensive groundwater monitoring plans are in place to track movement of S-ISCO chemicals and contaminant impacts, confirming that contamination is being oxidized, not mobilized.
- *Reduce Waste Production:* Because soil is treated in place and on site, no soil is removed for disposal.
- *Protect Land and Ecosystems:* S-ISCO destroys the contaminant source without removing soil or causing significant land disturbance. S-ISCO treatment often enables the full use of treated land for its intended purpose.

Attachment 1:

US EPA OSWER “Recommended Elements for Greener Cleanup, Environmental Footprint Assessments and Best Practices”

OSWER cleanup programs should consider these recommended elements when carrying out greener cleanup environmental footprint assessments and evaluating best practices that may be useful during the cleanup process.

1. Minimize Total Energy Use and Maximizes Use of Renewable Energy
 - Minimize energy consumption (e.g. use energy efficient equipment)
 - Power cleanup equipment through onsite renewable energy sources
 - Purchase commercial energy from renewable resources
2. Minimize Air Pollutants and Greenhouse Gas Emissions
 - Minimize the generation of greenhouse gases
 - Minimize generation and transport of airborne contaminants and dust
 - Use heavy equipment efficiently (e.g. diesel emission reduction plan)
 - Maximize use of machinery equipped with advanced emission controls
 - Use cleaner fuels to power machinery and auxiliary equipment
 - Sequester carbon onsite (e.g., soil amendments, re-vegetate)
3. Minimize Water Use and Impacts to Water Resources
 - Minimize water use and depletion of natural water resources
 - Capture, reclaim, and store water for reuse (e.g. recharge aquifer, drinking water irrigation)
 - Minimize water demand for re-vegetation (e.g. native species)
 - Employ best management practices for storm water
4. Reduce, Reuse, and Recycle Material and Waste
 - Minimize consumption of virgin materials
 - Minimize waste generation
 - Use recycled products and local materials
 - Beneficially reuse waste materials (e.g., concrete made with coal combustion products replacing a portion of the Portland cement)
 - Segregate and reuse or recycle materials, products, and infrastructure (e.g. soil, construction and demolition debris, buildings)
5. Protect Land and Ecosystems
 - Minimize areas requiring activity or use limitations (e.g., destroy or remove contaminant sources)
 - Minimize unnecessary soil and habitat disturbance or destruction
 - Minimize noise and lighting disturbance