



The Generation of **ACETONES** and **KETONES** – *a Positive Process?*

By **JIM MUELLER, PH.D.**, The Adventus Group

A look back at an in-depth study regarding an in-situ chemical treatment, which employed a fermentation process – and exceeded a laboratory's expectations.

When an impacted aquifer is amended with carbon, or heated, a small portion of the fermentable organic matter may be converted to a variety of ketones, including acetone or methyl ethyl ketone (MEK; 2-butanone). The processes might temporarily raise groundwater concentrations for such compounds above site-specific cleanup levels and also may trigger regulatory concerns, unless one completely understands the methods, fate and transport of ketone production.

Acetone is a VOC, but it also provides a readily biodegradable food source for soil microbes that perform reductive dechlorination. In groundwater, acetone generally has a half-life that varies from 19 to 197 days.^[1] On the other hand, MEK, one of the more common volatile ketone compounds, has been widely used as an

industrial solvent for paints, lacquers and varnishes in the past.^[2] It is also known for being highly degradable^[3] as its environmental half-lives have reportedly ranged from 13 to 128 days.^[1]

fermentation products is widely recognized as a potential limitation of substrate addition for enhanced bioremediation.^[5]

For instance, during a carbon injection, comprised of corn syrup and

“ During another case study reported by the same authors, elevated levels of MEK and acetone concentrations were detected in the injection well and several downgradient wells. ”

The occasional, transient production of acetone and/or MEK generally occurs when alkanes and high-organic carbon levels, which exist in sub-oxic, methanogenic environments, are present.^[4] It is assumed that MEK and acetone production transpires before the system actually becomes fully anaerobic, or after a carbon source is injected. The formation of such

cheese whey, that was followed by the bio augmentation example reported in the literature^[6], MEK was observed at concentrations of 3,200 µg/L, but was not reported in subsequent monitoring (with a detection limit of 100 µg/L). It was hypothesized that MEK was developed as a result of highly effective dechlorination reactions and was possi-

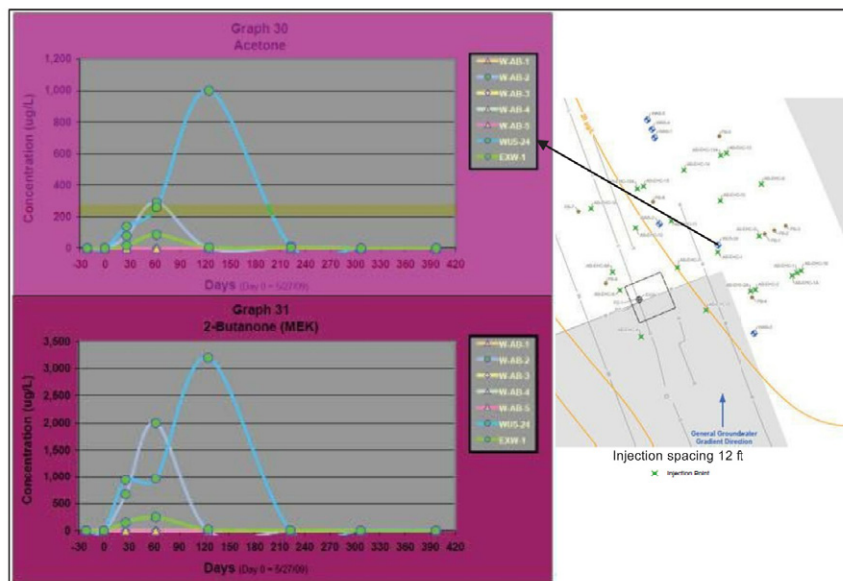


Figure 1: Site A - The treatment of chlorinated ethenes in a silty sand/clayey sand aquifer elevates acetone and MEK levels.

bly associated with the enhanced activities of *Clostridium* sp. or other ketone-producing fermenters that also dechlorinate ethenes. During another case study reported by the same authors, elevated levels of MEK and acetone concentrations were detected in the injection well and several downgradient wells, with initial levels as high as 6,000 µg/L. These concentrations rapidly decreased due to an extension of time and distance.

Meanwhile, acetone can also be generated abiotically. For example, it was produced as a result of electrical resistance heating (ERH) treatment at five U.S. Navy facilities.^[7] After ERH, acetone concentrations in groundwater are typically less than 500 mg/L, as acetone rapidly biodegrades to non-detectable levels while the site cools down to ambient conditions.

Other possible sources of ketones

There are several other circumstances in which MEK and acetone are observed in water samples from remediation sites:

- **Lab artifacts** – Acetone has also been produced in samples that were stored using standard preservation techniques. Volatile fatty acids (VFAs),

such as propionic acid, generated during preservation, can be biologically reduced to isopropyl alcohol (IPA). IPA then undergoes photocatalytic

oxidation as it converts to acetone. Such oxidation can occur during the entire duration of the sample hold time (between sample collection and analysis).

- **False positives** – Certain VFAs may be transformed into acetone during sample preservation and/or analytical processing. Some sources of carbon will generate large volumes of VFAs. For example, it is possible to convert acetic acid or other VFAs to acetone through the usage of high temperatures while packing in a column during GC analysis. It may even be feasible to convert VFAs to acetone during certain sample cleanup steps that are employed prior to GC analysis.
- **Metal oxides** – There is also evidence that some metal oxides can convert acetic acid into acetone; various aquifers actually have extensive amounts of native iron oxides.
- **Field activity contaminants** – Acetone may also be converted as a result of contaminants from field activities, such as residuals from cleaning equipment.

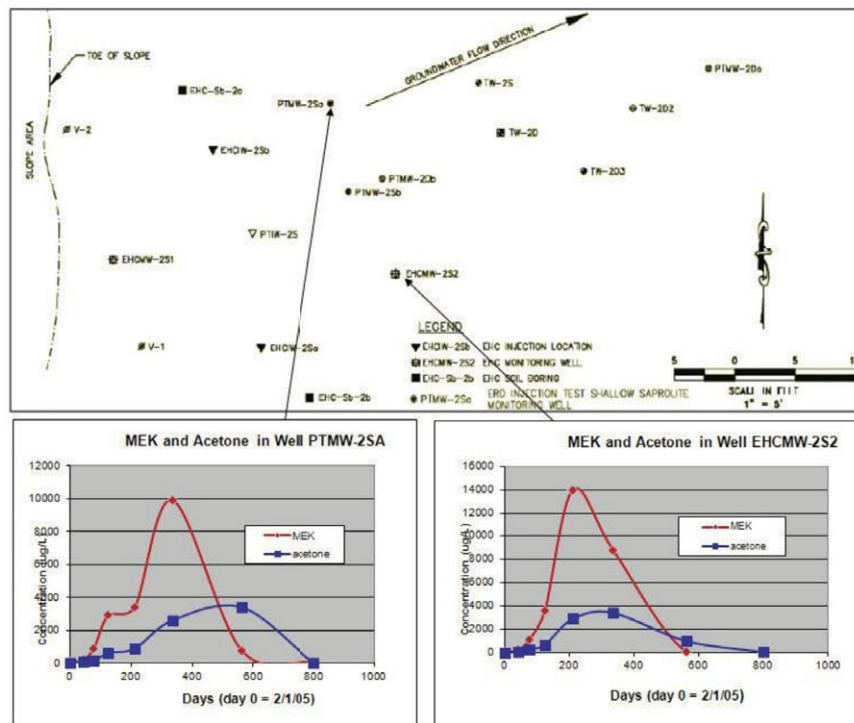


Figure 2: Site B - The treatment of chlorinated ethenes, ethanes, and methanes in a saprolite aquifer leads to increasing levels of acetone and MEK.

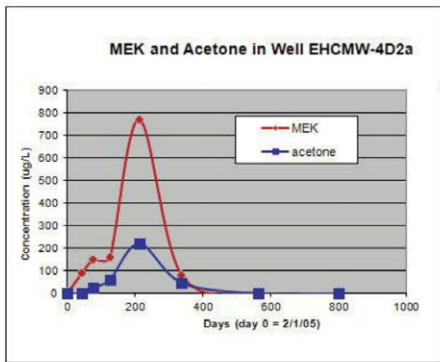


Figure 3: Site C - The treatment of chlorinated ethenes, ethanes, and methanes in a weathered bedrock aquifer raises acetone and MEK levels.

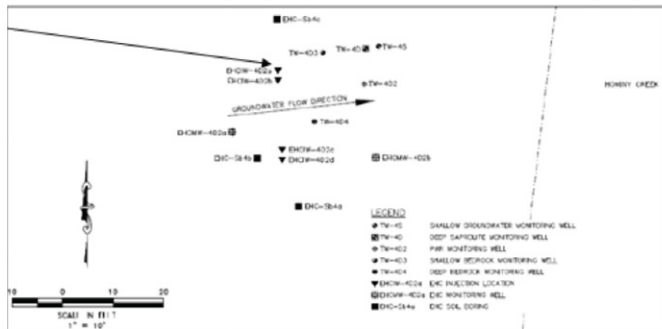


Table 1. Site E: Design of EHC ISCR.

EHC PRB dimensions:	Value	Unit
PRB length	200	ft.
PRB width	15	ft.
Depth to top of plume	6	ft bgs
Depth to bottom of plume	35	ft bgs
PRB thickness	29.0	ft.
PRB volume	87,000	ft ³
Mass of soil in PRB	5,003	U.S. tons
Estimated porosity	30%	
Volume pore space	26,524	ft ³
EHC mass calculations:		
Percentage EHC by soil mass	0.30%	
Linear groundwater velocity	0.16	ft/day
Contact time	94	days
Contact time * application rate multiplier	28	days*%EHC
Mass of EHC required	30,050	lbs.
Mass of EHC required per sq. ft. of face area	5.2	lbs./ft ²

• **Minor catabolites of zero valent iron (ZVI) reactions** – In iron literature, there are reports concerning the formation of small amounts of butane (C₄H₁₀) and butene (C₄H₈) during degradation of TCE and TCA, while using ZVI. Oxidation from butane to MEK may also occur.

of time, in which ketones were observed, ranged from two to 15 months, dependent upon site-specific conditions.

Site A. Chlorinated ethenes present in a silty sand/clayey sand aquifer, with a groundwater velocity of 5 ft/d was treated with EHC at 0.25 percent (soil mass basis). In one well near the up-gradient

acetone and MEK were elevated during the first three to 18-month-long period following the injection process (Figure 2). Subsequently, the concentrations remained below regulatory guidelines.

Site C. Chlorinated ethenes, ethanes and methanes were present in a weathered bedrock aquifer. For a period of three to 14 months after the injection, the concentrations of acetone and MEK were elevated in one well near the up-gradient edge of the injection zone (Figure 3). Thereafter, the concentrations remained below regulatory guidelines.

Site D. To treat chlorinated ethenes in a silt and silty sand aquifer, a 1 percent EHC application rate was applied during the PRB configuration. The concentrations of acetone and MEK were elevated for roughly five to 15 months after the injection occurred in multiple wells within and near the down-gradient edge of the injected zone (Figure 4). All concentrations remained below regulatory guidelines after the treatment.^[8]

Site E. Throughout September and October 2009, a 200-foot-long EHC-amended zone, situated perpendicular to the perceived groundwater flow direction, was created to control a cis 1, 2-dichloro-

Acetone was elevated above standards during the initial two to eight-month-long time period following the injection. Afterwards, the concentrations remained below regulatory guidelines.

Field data of ketone generation

The generation of ketones has certainly not been observed at every site where products, such as Adventus' EHC, have been utilized, yet some of these compounds have still been noted at times. Examples of temporarily elevated acetone and MEK concentrations are provided below, according to the following five sites. The distance of travel varied from nearly five to less than 100 feet down gradient, and the length

edge of the injection zone (Figure 1), the concentration of acetone was elevated above standards during the initial two to eight-month-long time period following the injection. Afterwards, the concentrations remained below regulatory guidelines.

Site B. EHC was applied to treat a plume containing chlorinated ethenes, ethanes and methanes in a saprolite aquifer. In two wells near the downgradient edge of the injection zone, the concentrations of

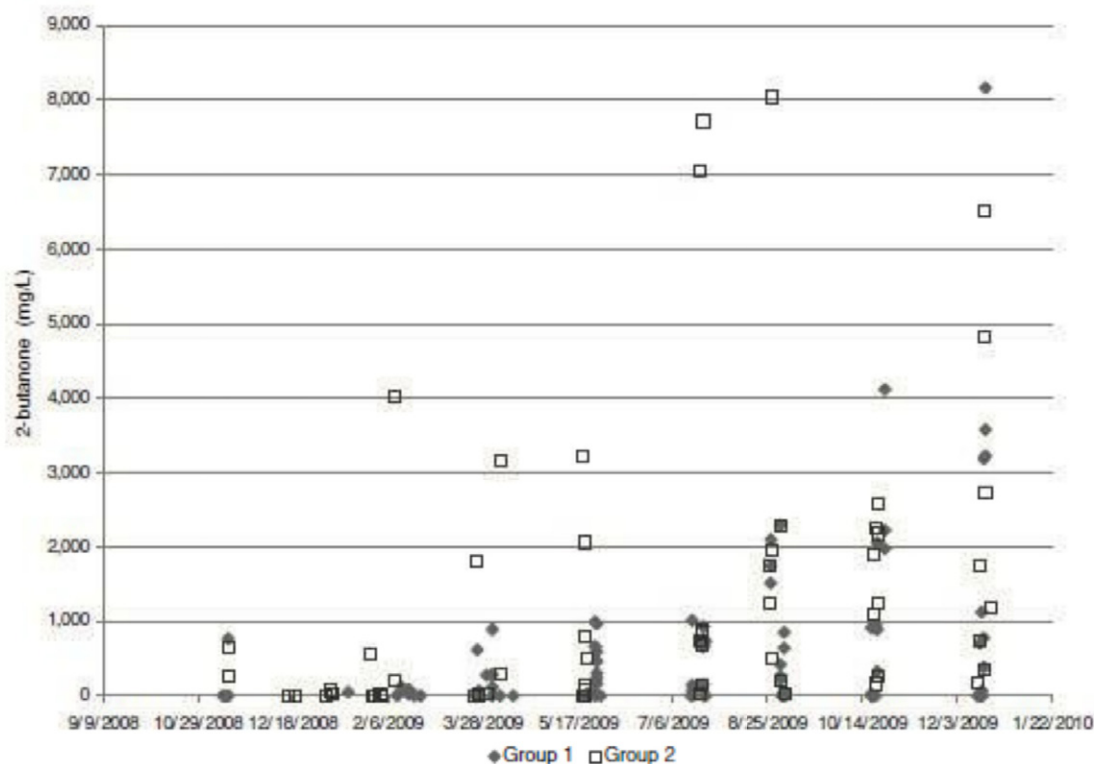



Figure 4: Site D - The treatment of ethenes in silt and silty sand aquifer further increases MEK levels.

ethene (cDCE) plume at a site in Northeast USA. The targeted depth interval ranged from 6 to 35 ft. bgs. The area received 30,050 lbs. of the amendment, which was applied to eight injection points (Table 1).

Following the injection via hydrofracturing, rapid and effective cDCE removal (without the accumulation of catabolites) was associated with the detection of MEK in wells YO-119 and YO-117D and, to a lesser degree, in wells YO-117S, YO-14ALX, YO-14X, and YO-12AX (Figure 5). Acetone generation was noted as a transient effect at YO-12AX during the March and June 2010 sampling events (Figure 6). Data from the two wells above indicated that the occurrence of MEK actually coincided with increases in concentrations of TOC and dissolved iron. Therefore, it is likely the MEK was produced due to enhanced microbial activity, which was influenced by the injected chemicals.

It should be noted that the injection contractor also used supplemental guar. As previously noted, guar is a readily biodegradable carbon source that could have contributed to the observed MEK response.



JEROME®
Toxic Gas Analyzers
Mercury | Hydrogen Sulfide

Jerome® findings are accepted by the EPA
On-Board Data Logging | 20,000 Data Points | 24 Hour Customer Support

ARIZONA INSTRUMENT LLC
800.528.7411 | www.azic.com | Made in the USA



Brazil is a BIG country.

Let SGW help you make it manageable.

Navigating the environmental opportunities in Brazil takes the skill of an explorer, the expert knowledge of a local guide, and the reliability of the best porters.

Find it all in the capable hands of SGW Services, Brazil's leading environmental consultancy, serving multinational clients to the highest international standards.

Whether you're a consultancy based in U.S. without operations in Brazil, or an industrial client searching for local and reliable alternatives for Brazilian plants, let SGW be YOUR local team.

Visit us online today at SGWservices.com or call 800-259-1292 (in the US) or 815-599-1280 (international) and discover all the ways SGW can help you make your entry into Brazil a little less intimidating.



The Soil & Groundwater Services Company

ACETONES and KETONES

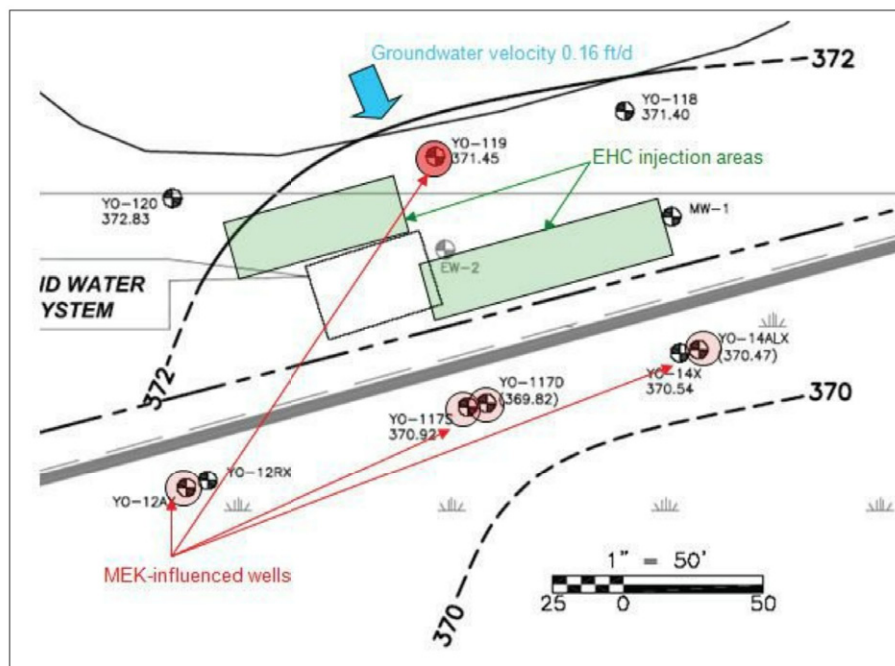


Figure 5. Site E - The location of monitoring wells and MEK impacts (red circles depict higher MEK; pink circles illustrate lower MEK).

Data from the July 2010 sampling event revealed the MEK concentration essentially decreased in well YO-119, demonstrating the transient nature of the phenomenon. Specifically, MEK concentrations stabilized or decreased at well locations YO-119, YO-117D and YO-12AX (Figure 6). However, based on the most recent data (samples collected on July 29, 2010), MEK concentrations had already been increasing at wells YO-14ALX and YO-117S prior to July 2010.

Analysis of site-specific degradation rates is not yet practical, but, based on the data in the downward slopes for MEK concentrations at YO-119 and YO-117D, it is possible to hypothesize half lives ranging from two to 14 days (using YO-119D data) or even upwards of 370 days (using YO-117D

data). According to a half-life range of 20 to 200 days (which is consistent with literature values discussed above), and assuming no further increases of MEK concentrations occurred (consistent with concentration trends at YO-119 and YO-117D), the June 2010 MEK concentrations would likely not drop below cleanup criteria for another three months to three years (Table 2). However, based on observations and experiences at other sites, the presence of MEK is expected to rapidly decrease and, consequently, will not be an issue throughout the next 12 to 18 months. Predictably, the MEK concentrations at this site were closely correlated with the TOC levels (Figure 7).

With respect to acetone detections on site, the data results were mixed. The

Table 2. Site E: Hypothetical Time for MEK to Drop from July 2010 Observed Concentrations to Below Standards.

	Well	MEK µg/L in June 2010	Number of Half-lives to Drop Below 5 µg/L	Time to drop below 5 µg/L (days)
			Half-life of 200 days	Half-life of 20 days
YO-119	480	7	132	1,317
YO-117D	320	6	120	1,200

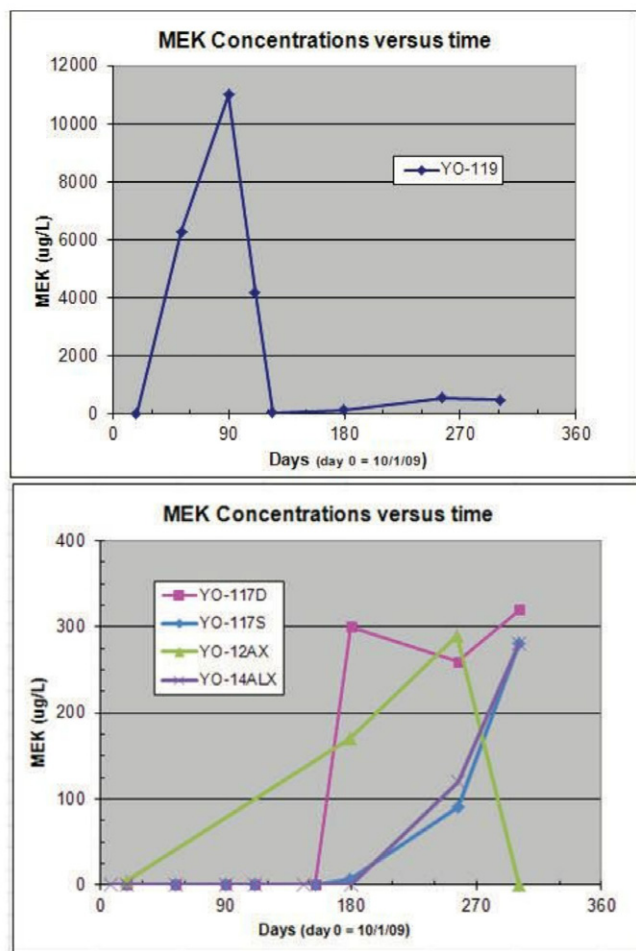


Figure 6. Site E - MEK time histories

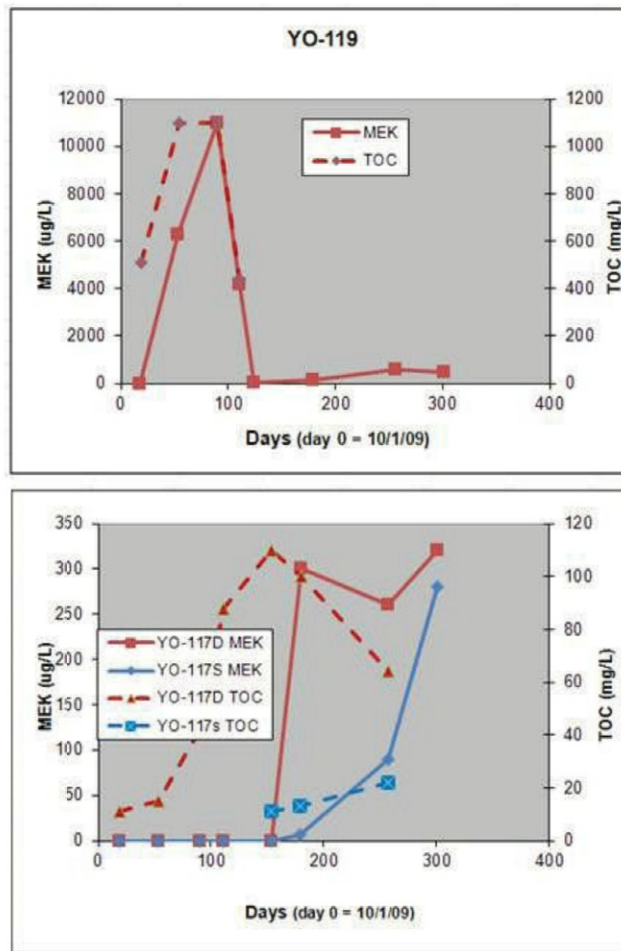


Figure 7. Site E - MEK and TOC

historic acetone data at down gradient wells depicted sporadic hits above the 5 µg/L performance standards, with a maximum of 50 µg/L detected in April 2001 at YO-12A. More typical detections are within the range of 5 to 16 µg/L. While these detections are not conclusively linked to any one process, acetone was detected in several other wells during the April 2001 round of sampling as well, suggesting those results may have been associated with lab contamination. The monitoring area consisted of wetlands, which may provide sufficient TOC for naturally occurring processes to generate acetone. Nevertheless, it is presumed the acetone detected in March and June 2010 at YO-12AX, with concentrations of 71 µg/L and 80 µg/L, respectively, was developed through

chemical additions and subsequent fermentation processes. **PE**

For more information, please visit www.adventusgroup.com.

EHC is a registered product name from the Adventus Group.

References

1. Aaronson, D. and P.H. Howard. 1997. Anaerobic Biodegradation of Organic Chemicals in Groundwater: A Summary of Field and Laboratory Studies, Prepared for: American Petroleum Institute, Chemical Manufacturer's Association, National Council of the Paper Industry for Air and Stream Improvement, Edison Electric Institute, and American Forest and Paper Association.
2. Lurie, A.P. 1967. Ketones IN Kirk - Othmer Encyclopedia of Chemical Technology, Vol. 12. John Wiley & Sons, NewYork, pp. 101-169.
3. Devinny, J.S., M.A. Deshusses, M.A., and T.S. Webster. 1999. Biofiltration for Air Pollution Control. Lewis Publishers, New York.
4. www.navy.mil/Archive/emdq-2005/2-3-1.pdf
5. ESTCP, 2010. Final Report - Loading Rates and Impacts off Substrate Delivery for Enhanced Anaerobic Bioremediation. ESTCP Project ER-0627, Bruce Henry, Parsons, February 2010.
6. Suthersan, S. S. and F.C. Payne. In Situ Remediation Engineering, page 133.
7. Beyke, G. and D. Fleming. 2005. In Situ Thermal Remediation of DNAPL and LNAPL Using Electrical Resistance Heating, REMEDIATION Summer 2005.
8. Peale, J.D.G., J. Mueller and J. Molin. 2010. Successful ISCR-enhanced bioremediation of a TCE DNAPL source utilizing EHC and KB-1. Remediation Journal, Vol. 20 Issue 3, Pages 63 - 81.