

MEASURING CHEMOX APPLICATION SUCCESS!

Douglas D. Carvel, P.E., President, MECX LLC, 6300 West Loop South, Suite 500, Bellaire, TX 77401, 713-585-7003, doug.carvel@mecx.com and Richard T. Cartwright, P.E., CHMM (MECX LLC, Buffalo, NY, USA)

Abstract: Be assured, “CHEMOX Treatment of Organics in the Saturated Zone” works. In fact, for every project in which CHEMOX has been applied in the saturated zone, the total mass of organic contamination at the site has been reduced. The fundamental question should not be, “Did the technology work?” but instead, “How effective has the treatment been?” This question can only be answered by accurate and complete pre-treatment and post-treatment contaminant mass characterization, which on most sites has almost never been performed.

Introduction. In-situ application of Chemical Oxidation (CHEMOX) mass destruction technologies including, Fenton’s Reagent, Ozone, Permanganate, Persulfate and Peroxide have all been too easily maligned during the last 10 years of technology development for being ineffective remediation treatment technologies. This pre-assumed ineffectiveness bias is based on 1.) Apparent inadequate dissolved contaminant reductions or even possible increases in either target constituents or reductive byproducts in the dissolved phase, and 2.) Post-treatment dissolved phase contaminant rebound. Reality is that total mass reduction has actually occurred. However, because these sites have not been properly characterized to assess the true nature and distribution of contaminant mass, fully effective reagent application and subsequent evaluation of these aggressive remediation approaches have not been performed.

Incomplete or inaccurate characterization may not seem that important for sites where traditional mass transfer technologies have been and are still being used. However, it is essential for the application design and subsequent evaluation of CHEMOX Technology remediation sites. Typically for mass transfer technologies, if the site investigation was incomplete or inaccurate, it has generally been regarded as acceptable to just keep operating for an additional 2-5 years after the originally estimated treatment time of 10-15 years. However, for an oxidation technology application site where the treatment time may be as little as one or two weeks, effective system design and reagent application is absolutely necessary. Therefore, accurate and complete site pre and post treatment characterization of CHEMOX Technology remediation sites is a definite must.

Total Mass Evaluation is Required, Dissolved Phase Evaluation alone is Inaccurate. For traditional mass transfer technologies, use of only dissolved phase mass characterization techniques to measure relative concentrations of contaminants at the Site has generally been effective because the equilibrium conditions for the system remain constant relying on relatively static partitioning characteristics of the organic contaminants. This is acceptable, if the most of the total mass resides in the saturated zone and the groundwater elevations are static. Unfortunately at most sites, the groundwater is not static, smear zones of LNAPL sorbed contamination and in some cases phase separated pockets of DNAPL also co-exist. In these cases, a mass evaluation even for a mass transfer technology is essential for an effective system design.

Regarding the issue of apparently encountering ineffective in-situ CHEMOX applications, a mass evaluation is imperative because these treatments result in exothermic chemical and physically aggressive reactions, which affect the equilibrium conditions at the Site. These actions by themselves transfer sorbed and phase separated mass into solution, thus increasing the dissolved concentrations but not increasing the total mass. Through both physical and mechanical means these technologies convert sorbed mass and phase separated mass within and above the saturated zone into dissolved mass where it can be efficiently oxidized. In many cases, due to nature of the local site geochemistry, hydrogeology and technology application efficiencies more mass can be converted to dissolved mass than is oxidized. The result is that immediately after treatment and for several months later, even though the total mass has been reduced by orders of magnitude, the dissolved constituents may have increased. However, once the site returns to equilibrium, which could be several months, the actual reduction in total mass will be reflected in the dissolved mass. If a complete characterization of the nature and extent of the total mass in the treatment area had been completed, the success of the treatment would have been realized immediately.

Rebound Impossibility, Poor Site Characterization the Reality. The notion of isolated dissolved phase rebound being caused solely by an oxidation technology is absurd. Even if no treatment occurred, just the addition of the chemicals will cause the concentrations of the target contaminants to decrease through mere dilution. The only way that rebound can occur is if 1.) Contamination existing outside the treatment area migrates into the application area after treatment, 2.) Contamination exists as an undetected NAPL plug either within or outside the treatment area, and/or 3.) Leachable levels of sorbed contamination exist in the soils above the treatment area. All of these issues are associated with inadequate characterization of the Site and not an apparently ineffective application of the oxidation treatment.

Information Required for Characterizing Candidate Sites. To avoid the pitfalls described above and to ensure the success of any oxidation process application, three primary factors characterizing the true nature of the Site must be accurately identified and completed. These three factors are required for accurately evaluating a Site, designing an effective In-situ CHEMOX Treatment, and evaluating the success of the application. These three factors are: 1.) Nature of the contamination – How is the Mass distributed throughout the saturated zone, dissolved, sorbed and does it exist as a NAPL above or below the treatment area? 2.) Extent of the contamination – Where are the limits of the various phases of contamination in the soil and saturated zone including smear zones and NAPL? and 3.) Is the Source Known? - Where are the unsaturated and saturated zone source areas?

If all of these factors are not well defined, in-situ CHEMOX applications are likely to be regarded as a failure because the site will likely have unimpressive or misunderstood results with likely recontamination over time from plume migration. The following are recommendations for evaluating a site prior to designing and applying In-situ CHEMOX Reagent and for post treatment evaluation.

Remember it's the Mass, Remember it's the Total MASS. Traditional intrusive soil boring and monitoring well investigations combined with soil gas surveys, is typically acceptable for defining the source and extent of sorbed and dissolved contamination. They do not however, adequately define the mass distribution throughout the treatment area or the nature and extent of NAPL. Traditional sampling protocols rarely addressed the contaminant mass distribution throughout the entire saturated and unsaturated soil column. Since oxidation

technologies address all phases of contaminants and convert sorbed and phase separated mass into the dissolved phase during treatment, an understanding of the total mass in both the saturated and unsaturated zone is essential. The most cost effective and accurate method for obtaining this information is through geoprobe sampling within the treatment area before and after treatment. It is important to try to locate post treatment sampling points within a reasonable proximity to the baseline direct push points to attempt to replicate as nearly as possible the baseline results. This geoprobe sampling must be performed throughout the entire unsaturated and saturated contaminated soil column to determine the entire mass to be treated.

NAPL characterization is very problematic. NAPL distribution in both the confined and unconfined condition is accurately estimated through geoprobe sampling. Use of monitoring well data for LNAPL thickness estimates in the unconfined condition can be also a good representation of actual NAPL mass. However in confined applications, monitoring well data for LNAPL thickness is usually over stated and should be confirmed through geoprobe or downhole geophysical methods. Monitoring well data for all DNAPL sites should be confirmed through direct push sampling or geophysical tools.

Example Site Overview. The “Example Sites” cited below used direct push sampling procedures for Site delineation, Source Area Identification, baseline treatment area characterization, and post treatment monitoring. Monitoring wells were used to determine dissolved phase concentrations for both pre and post treatment. These Sites were selected because they are typical of most gasoline and dry cleaner sites found in the coastal regions of the USA. Figures A-1 through A-3 are for the Example A Site and Figures B-1 through B-3 are for the Example B Site. Figures A-1 and B-1 present a table that includes critical data for each Site. The second figure presents the trend of total mass distribution before, during and after treatment. The third figure presents information on the behavior of the degradation products DO and CO2.

Example A - DNAPL Chlorinated Solvent Site

The DNAPL Site is a typical dry cleaner Site in low permeability silty clay. Depth to groundwater is 15 feet below ground surface. No phase separate chemicals were observed. As shown on the figures, a large amount of mass reduction was achieved after treatment. This mass reduction was not initially reflected in the dissolved concentrations. In fact, the dissolved concentrations were only observed to decrease after the site reached equilibrium. All sampling was performed through direct push methods and the use of fixed monitoring wells.

Figure A-1							
FENTON'S REAGENT TREATMENT							
EXAMPLE CHLORINATED VOC MONITORING PROGRAM							
PROGRESSIVE SAMPLING RESULTS (mg/L)							
SAMPLE PERIOD	Dissolved VOCs	Sorbed VOCs	DNAPL	TOTAL MASS	PERCENTAGE REDUCTION	ORP mV	CO2
BASELINE	2	220.0	0	222	0	35	20
14 DAYS	21	2.1	0	23.10	89.6	250	290
30 DAYS	19	2.6	0	21.60	90.3	230	240
60 DAYS	5	17.9	0	22.90	89.7	90	210
90 DAYS	0.2	20.6	0	20.8	90.6	35	190
<u>SITE CHARACTERISTICS</u>							
PCE, TCE, TCA							
SILTY CLAY							
15 FEET OF SATURATE ZONE							
NO SMEAR ZONE							
10 FEET OF DEPTH TO GROUNDWATER							

Figure A-2
CHLORINATED SOLVENT SITE
MASS DISTRIBUTION

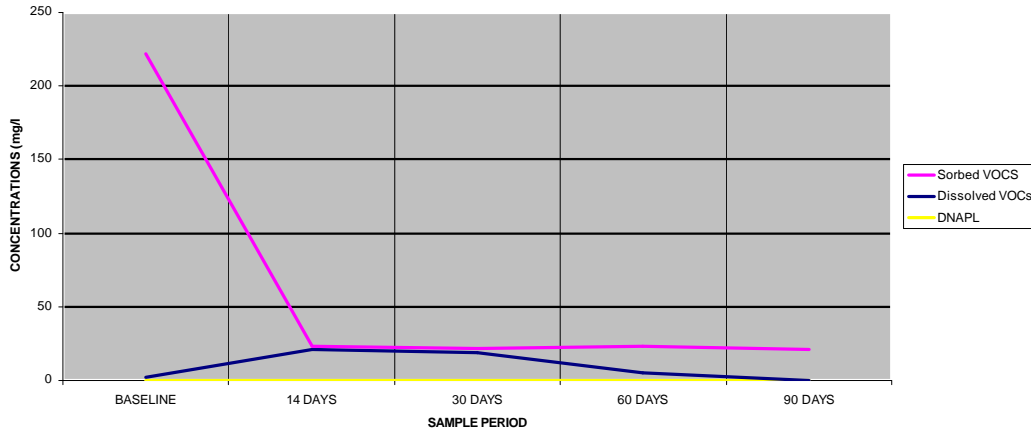
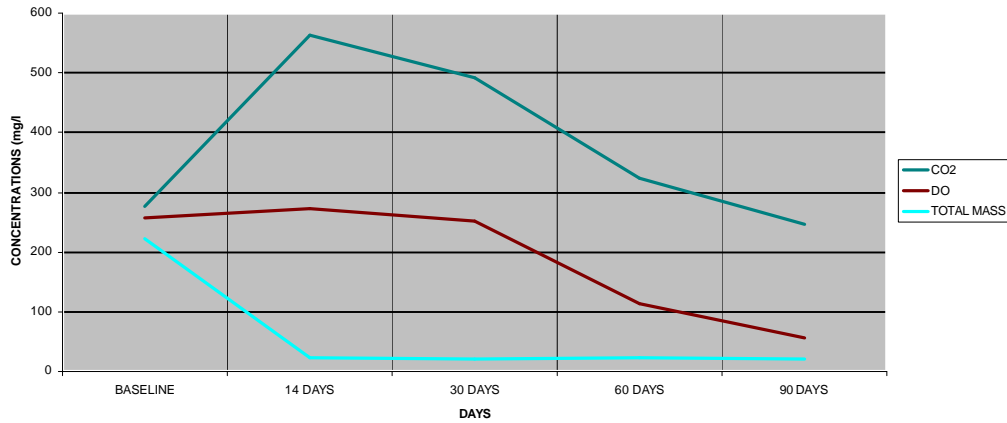


Figure A-3
CHLORINATED SOLVENT SITE
DO/CO₂



Example B - LNAPL Petroleum Hydrocarbon Site

The LNAPL Site is a typical former Gas Station Site in low permeability silty clay. Depth to groundwater is 15 feet below ground surface. Phase separate chemicals were observed and a smear zone existed due to seasonal variability in water table elevation. As shown on the figures a large amount of mass reduction was achieved after treatment. Note that this mass reduction was not initially reflected in the dissolved concentrations. In fact, the dissolved concentrations were only observed to decrease after the site reached equilibrium. All sampling was performed through direct push methods and the use of fixed monitoring wells.

Figure B-1							
FENTON'S REAGENT TREATMENT							
EXAMPLE PETROLEUM HYDROCARBON SITE							
PROGRESSIVE SAMPLING RESULTS (mg/L)							
SAMPLE PERIOD	Dissolved TPH	Sorbed TPH	LNAPL	TOTAL MASS	PERCENTAGE REDUCTION	ORP mV	CO2
BASELINE	0.2	22.0	1000	1022.2	0	35	20
14 DAYS	100.2	15.0	0	115.20	88.7	250	290
30 DAYS	35	18.0	0	53.00	94.8	230	240
60 DAYS	5	15.0	0	20.00	98.0	90	210
90 DAYS	0.3	2.8	0	3.1	99.7	35	190
SITE CHARACTERISTICS							
JET FUEL							
SILTY CLAY							
15 FEET OF SATURATE ZONE							
NO SMEAR ZONE							
10 FEET OF DEPTH TO GROUNDWATER							
LNAPL MASS IS EQUILANT TO 6 INCHES OF FREE PRODUCT							

Figure B-2
PETROLEUM HYDROCARBON SITE
TOTAL MASS DISTRIBUTION

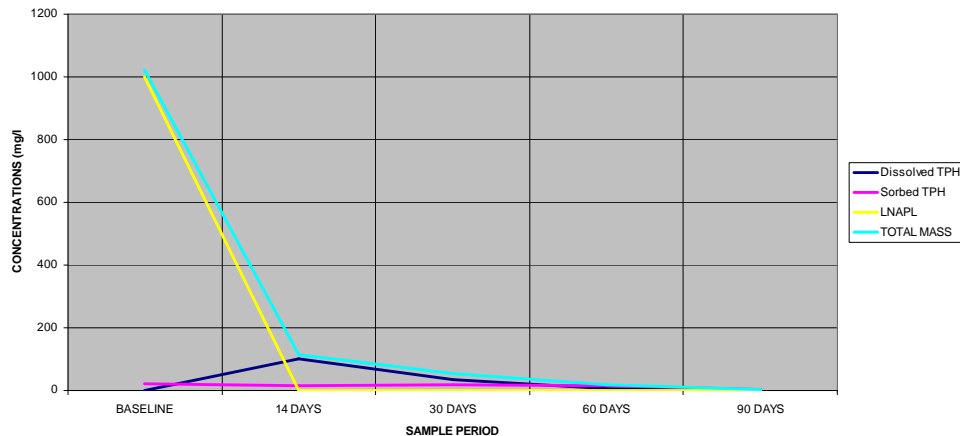
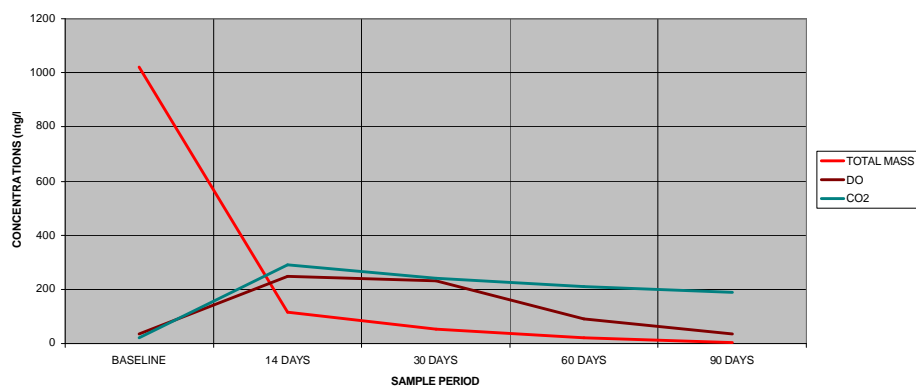


Figure B-3
PETROLEUM HYDROCARBON SITE
DO & /CO₂



Summary and Conclusions. CHEMOX Technologies are contaminant mass destruction processes and as such require an accurate and complete evaluation of the source location, nature and extent of the contaminant to successfully apply these technologies.

CHEMOX Technologies alter the equilibrium partitioning of total mass distribution by converting sorbed and phase separated mass to dissolved phase both during and for a period of time after the application of treatment reagents. For this reason, evaluation of the success of the treatment application cannot be based on dissolved phase concentrations alone. Full evaluation of the sorbed and phase separated mass throughout the entire soil column, saturated and unsaturated, is required for an accurate design and evaluation of the technology.