Amec in July 2014 conducted a field test of anaerobic biodegradation to support the anaerobic EBR modeling that was performed as part of the ST012 RD/RAWP due to the fact that significant assumptions were made in the modeling/analysis (Addendum #2, Appendix C, page 1-1, lines 156-158). This field test was comprised of two push-pull tests performed at existing wells W-11 and W-30, both of which are completed in the lower saturated zone, and both of which were known to be impacted by LNAPL. The purpose of the field test was to determine sulfate utilization rates. Pumping rates during the extraction phase from W-30 could not be sustained due to well fouling, and the limited amount of groundwater extracted from W-30 'did not provide a sufficient data set to estimate sulfate utilization' (lines 475-476). At W-11, sulfate concentrations increased during the pull portion of the test, which 'indicate that background groundwater sulfate concentrations were being pulled into the well and prevent the accurate estimation of sulfate utilization' (lines 477-478).

Instead, sulfate utilization was estimated from the shut-in portion of the test. Data presented from W-11 show that the TPH and benzene concentrations remained essentially constant during the shut in period (Table 2-1), while normalized sulfate concentrations were greater than the normalized tracer concentrations during most of the shut in phase of the test (Graph 3-4). Thus, very little sulfate utilization was demonstrated from the results at this well.

Data from W-30 show that the DRO and TPH concentrations increased substantially during the shut-in period of the test and benzene concentrations approximately doubled (Table 2-2), while the sulfate concentration decreased exponentially with time (Table 2-6). While the results at this well showed sulfate utilization during the shut in period (Graph 3-5), the results did not demonstrate that TPH or benzene were consumed by the sulfate that was utilized.

Based on the conflicting data obtained during the field test, it is recommended that further field and/or laboratory testing be completed. In light of the inconclusive results on benzene degradation accompanying sulfate utilization, the first objective of the additional site specific testing should be demonstrating that the sulfate-reducing microbial consortia at this site ~~is~~ are capable of degrading benzene, and if so, what conditions are necessary to maximize the degradation rate. The extremely high sulfate injection rate proposed in Addendum #2 should be investigated in the laboratory to determine what the 'shock loading' of sulfate will do to the microbial populations, and the geochemical changes this sulfate addition will cause. Laboratory experiments could determine if the existing microbial system is deficient in sulfate, and if so, the amount of sulfate needed to maximize degradation rates. Based on what is learned from the laboratory experiments, a field test can be designed that will allow estimation of field degradation rates of benzene (if benzene is found to degrade), using a flow-through field setup rather than a push-pull test. Estimates of benzene degradation derived from the field test can be used in the model to estimate treatment times, although it must be kept in mind that, "***Anaerobic bioremediation is still not thoroughly understood, especially under field conditions, making clean-up times difficult to predict***" (ESTCP, 1999). The presence of significant LNAPL at this site and low permeability zones that are known to contain LNAPL will limit the biodegradation rate (ESTCP, 1999, page 6).

Commented [WU1]: "Modeling results for both processes indicated that the remediation goals could be met; however, there were **significant assumptions made for the anaerobic approach.**"

Commented [WU2]: Likely due to enhanced microbial activity in response to injectate, and indicative of likely problems with well fouling in the full-scale effort.

Commented [WU4]: Granted, it can be difficult to demonstrate degradation of a particular compound, and calculate rates, without isotope studies. But the push-pull pilot study really didn't show anything useful – except that fouling is a problem.

Commented [WU5]: Generally, as we told AF almost a year ago: "The results of the EBR Pilot Test are equivocal, difficult to interpret for practical use, and result in high uncertainty when used to model and plan full-scale EBR, and MNA." (CSS: *Review of Documents for Operable Unit 2, Site ST012, at the Former Williams Air Force Base, Mesa, AZ* May 17, 2016)

Commented [WU6]: If sulfate is depleted (and it is, where COCs exist), then sulfate is limiting in some way. It is entirely reasonable to assume that some added electron acceptor would be useful, since there is a huge mass of electron donor (i.e. the petroleum LNAPL). I can't argue with AF choosing sulfate over oxygen, since adding sufficient oxygen would be a huge endeavor, whereas adding sulfate is relatively easy. But a lab study, using subsurface samples from sulfate-depleted zones with LNAPL present, could give an idea of the response of the system to added sulfate.

I do tend to lean toward field studies rather than lab studies, though. And rates determined in lab studies often don't translate well to the field reality. But a lab study showing that sulfate reducers responded strongly to sulfate addition, and BTEX disappeared, would be encouraging.

Commented [WU7]: It's still going to be tricky to determine the amount needed to maximize degradation rates. I would rather emphasize the more uniform distribution of a moderate range of sulfate concentrations; that is, more injection points, lower injectate concentrations.

Commented [WU8]: *Estimates of benzene degradation derived from the field test* can be used as long as the complexity of LNAPL/GW (i.e., LNAPL as a continuing source to be depleted) is taken into account. That is, the model should not assume that COCs are immediately, consistently, and always available in the groundwater (available for degradation) as long as some COCs remain in LNAPL.

These estimates of degradation rate are always for benzene in GW, not for the totality of benzene in LNAPL and in GW – so the rate estimates are strictly applicable only to benzene in GW. The movement of COCs from LNAPL to GW, so as to be available for degradation, is a whole different matter, ratewise.

Table 2-5 Concentrations of Solution Used for Injection

Location	Bromide Concentration (mg/l)		Sulfate Concentration (mg/l)	
	Calculated	Lab Result	Calculated	Lab Result
ST012-W11	150	150	4,300	2,300
ST012-W30	150	220	4,300	3,800

Notes:
mg/l – milligrams per liter

Figure [SEQ Figure * ARABIC] Note that the sulfate injectate concentrations used for the pilot test are in the low thousands ppm, instead of the high hundreds of thousands ppm proposed for full-scale EBR. Therefore the pilot test cannot be considered as representative of the full-scale effort proposed in terms of sulfate reagent concentrations.

Commented [WU3]: As Eva noted, AF needs to show how the high injection concentrations will affect microbiological activity – further testing could provide this info. They plan for sulfate to eventually be distributed throughout much of the site at fairly reasonable levels (low thousands ppm), but still substantial portions of the site around the injection areas will have very high GW concentrations of sulfate for quite a while.

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The laboratory and field tests would also be used to determine the sulfate dosing required to degrade benzene. According to the referenced ESTCP document, "***Ground water contaminated from gasoline contains not only BTEX compounds, but many other gasoline components as well. At the Seal Beach site, much of the injected nitrate and sulfate was utilized by bacteria to degrade non-BTEX hydrocarbons. This makes it difficult to predict the amount of electron acceptor(s) that will be needed for complete BTEX removal.***" In field experiments at a gasoline spill site, Reinhard et al. (ES&T, 31(1):28-36, 1997) found that only 13 to 40% of the sulfate consumed was used to degrade BTEX. However, review of Addendum #2 shows that the current implementation plan for EBR at ST012 estimates the sulfate dosage required by assuming that only enough sulfate is needed to degrade BTEX, disregarding the other components of the jet fuel, and does not include BTEX in the LPZ. Thus, the planned injection of 870 tons of sulfate – as large as this amount is – is still extremely short of what would be required to degrade the BTEX at ST012.

Commented [WU9]: **Addendum #2, Lines 822-827:** "Initial target TEA dosage is based on treating approximately 30% of the LNAPL mass in the CZ, UWBZ, and LSZ, on treating approximately 30% of the LNAPL mass in the CZ, UWBZ, and LSZ, accounting for the likelihood that BTEX+N will be preferentially consumed during bioremediation over longer chain hydrocarbons. Although BTEX+N are the primary COCs, other compounds will degrade and consume sulfate in the process."

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Evidence from Other Sites

First, AF should provide well-documented case studies of specific sites where EBR, as AF plans to do it, has actually remediated 100s of thousands of gallons of LNAPL/BTEX so as to reach 500-600 ug/L BTEX in groundwater, with no LNAPL remaining (or, at least, no LNAPL with COCs in the LNAPL).

Lab Work, Initial Testing, etc.

Could do, as suggested above, some lab studies to see reactions of the indigenous microbes to high sulfate/salinity; changes in populations (of sulfate reducers, particularly, to see if population drop sharply, rebound, etc.) and if TPH and the COCs are degraded over time. Use subsurface media samples (each sample with matrix, groundwater, LNAPL; use replications to establish variability of results) taken from the location where the Field Study is to be done.

Commented [WU10]: *2016-10-25 - wafb ADEQ evals - usaf RTCs dated 8-22-2016 for ST012 Draft Final Add2- EBR RDRA WP-OU2- - see also FPU16-230 -- FPU17-089.pdf* had some useful comments about the microbiology.

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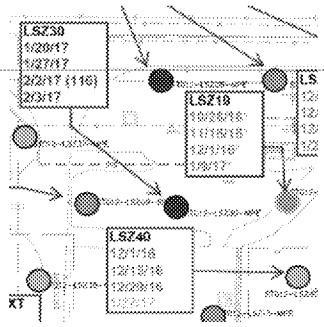
Field Study

Perhaps we should ask for a field study that involves actually remediating an LNAPL mass – that is, pick a well with substantial LNAPL, put a transect of injection wells upgradient of the LNAPL well, and a transect of monitoring wells immediately downgradient of the well, and inject sulfate, etc.,



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as planned for the full-scale EBR. - If AF can timely remediate that well so that no LNAPL is found in the well, and the COC concentrations in that well and the downgradient monitoring transect are below standards, then that would be strong evidence that a full-scale approach could work.

The chosen LNAPL well should have significant LNAPL – more than a sheen – at least two inches of LNAPL fairly consistently, so that actual *remediation of LNAPL* can be assessed.

> Note that my sense of where AF is going is that eventually they will claim that they don't actually have to get rid of LNAPL, but merely get GW concentrations of BTEX down to MCLs, "eventually". Encapsulation of LNAPL by microbial films (to degrade the BTEX moving from LNAPL to GW), by iron sulfide precipitates (to reduce flux of BTEX from LNAPL to GW), fouling and precipitates in and around LNAPL bodies (so that GW doesn't really flow close to the LNAPL) are things that could cause GW concentrations of BTEX to fall, while much BTEX remains in the remaining LNAPL. Hence my continued insistence on the idea that the details of performance monitoring make a huge difference in what "success" is.

Chosen well should be at elevated temperature, to correspond with the general site conditions.

Reagent injections (sulfate, etc.) should reflect those concentrations, rates, volumes, etc. that are proposed for full-scale EBR.

Assuming the field study continues for at least a year, the changes around the injection wells in terms of microbiology, sulfate concentrations, sulfide production, hydrogen sulfide generation, precipitation of iron sulfides, possible aquifer plugging, changes in pH, etc., can be monitored and evaluated for viability of a full-scale remedy, and any likely dangers, showstoppers, etc.

Fouling should be assessed for all wells (injection, LNAPL, monitoring), to determine the likely needs for well reworking, refurbishing, eventual replacement, etc. This is particularly important for the follow-on contractor (after AMEC's contract expires) to have an idea of long-term costs, and how to bid.

The downgradient monitoring transect can not only monitor COC changes, but also assess the geochemical footprint of downgradient locations, which would be pertinent to evaluating possible enlargement of a sulfate/etc. plume at full scale.

> Also, the distribution and concentrations of sulfate achieved downgradient of the injection transect is of great interest. The AF model indicates they can get a reasonable (to them) sulfate distribution, but reality in subsurface environments is often different from the models. The field study should designed to provide suitable data to design injection well spacing, injection rates, injection concentrations, pressures, etc., so as to achieve useful sulfate concentrations across the site.

Commented [WU11]: Note that AF intends to get the COCs down to 500-600 ug/L so that MNA can complete the remediation to MCLs in the required timeframe.

Of course that means that the MNA part is also significantly uncertain (i.e., a whole different bag of uncertainty), even if EBR performs just like AF models it.

Commented [WU12]: AF has consistently denied EBR is planned for LNAPL source remediation, and consistently affirmed that indeed EBR will remediate LNAPL source materials. But if AF is not going back to SEE (or other actual source remediation technology – "actual" meaning in a few years, not some indefinite long-term "eventually"), then EBR has to remediate the LNAPL, and do it right away with minimum hiccups. So the field study should explicitly confirm that a significant mass of LNAPL has indeed been remediated (or not).

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