Message

From: Dan Pope [DPope@css-inc.com]
Sent: 2/27/2017 8:43:11 PM
To: Davis, Eva [Davis.Eva@epa.gov]; d'Almeida, Carolyn K. [dAlmeida.Carolyn@epa.gov]
CC: Henning, Loren [Henning.Loren@epa.gov]; Wayne Miller (Miller.Wayne@azdeq.gov) [Miller.Wayne@azdeq.gov]
Subject: Sulfate Distribution
Attachments: removed.txt

At 1990 days (~5.5 years) after injections the AF model shows some areas up in the tens of thousands of ppm sulfate. They're setting up the injections and sulfate distribution (with injection/extraction) so that natural movement of the GW will take the sulfate (in fairly useful concentrations) throughout the site.

ST012_RDRAWP_ADDENDUM2_RTCs.pdf
Air Force (AF) Response to Comment (RTC)
Item 3

EPA reviewers indicated: "The sodium sulfate amendment has the potential to significantly increase the salinity of the water, and the Addendum 2 RDRA Workplan has not addressed this."

AF replied: "The EBR injections will increase salinity of the groundwater in the treatment area. The only applicable standard identified relating to salinity is a secondary maximum contaminant level (MCL) for total dissolved solids (TDS) of 500 mg/L. Secondary MCLs are established for nuisance conditions, not for the protection of public health. Fresh water typically has TDS values up to 1,000 mg/L or higher depending on the reference. Background TDS concentrations have not been characterized at ST012. From the groundwater model concentration transport figures showing sulfate for each zone in Appendix E, the injected concentration of

sulfate reduces by approximately two orders of magnitude in most areas of the site over a period of about five years and reduces by approximately one order of magnitude in the worst case areas (vicinity of UWBZ injection wells) over five years. Assuming most of the sulfate is converted to sulfide by the EBR process (removing oxygen mass from quantified TDS concentrations), assuming the sulfide does not precipitate (a conservative assumption), and accounting for the sodium component of the injected sodium sulfate solution, the remaining TDS would be about 80% by weight of the sulfate concentrations shown on the figures in Appendix E. Generally, a three orders of magnitude reduction from injected concentrations is necessary to approach the secondary MCL for TDS. Based on this information it is reasonable to project that salinity (as TDS) will be less than 1,000 mg/L and will approach the secondary MCL, depending on background TDS, over the vast majority of the site within the remedial timeframe (20 years post RODA 2). However, it is possible that some localized areas will have higher concentrations (e.g., up to 5,000 mg/L TDS). This discussion will be added to Section 3.3."

Sulfate reducers (and lots of other bugs) can live at amazingly high salinities. Of course, I don't know what bugs are at the WAFB site, nor how quickly suitable populations of sulfate reducers might develop after being hit with high sulfate concentrations, but bug are pretty resilient, especially in complex subsurface environments with lots of niches.

http://aem.asm.org/content/73/7/2093.full

Diversity, Activity, and Abundance of Sulfate-Reducing Bacteria in Saline and Hypersaline Soda Lakes

"Soda lakes are extreme environments with pH values up to 11 and salt concentrations up to saturation. These high pH values are maintained due to the high buffering capacity of sodium carbonate/bicarbonate, which are among the major anions in solution. The salinity can vary from 5 to 30 g/liter for hyposaline lakes to up to 500 g/liter for hypersaline lakes. Despite these extreme conditions, soda lakes are highly productive and harbor diverse microbial communities (6, 11, 25, 35) responsible for the element cycling.

The sulfur cycle, driven by haloalkaliphilic sulfur-oxidizing bacteria (SOB) and sulfate-reducing bacteria (SRB), is one of the most active element cycles in soda lakes...."

Also, for the sulfate distribution questions:

ST012_RDRAWP_ADDENDUM2_RTCs.pdf
Air Force (AF) Response to Comment (RTC)
Item 5

EPA reviewers indicated: "It appears that dispersion is to be relied on to distribute sulfate throughout the area to be treated, as groundwater flow lines for the injected sulfate solution shown in Figures E-1, E-8, and E-15 do not cover most of the areas on known LNAPL contamination.. The series of model results presented in Figure E-2 to E-7, E-9 to E-14, and E-16 to E-21 show the sulfate distribution (above background concentrations) for each of the vertical treatment zones, and appears to show that the sulfate is expected to move almost the same distance laterally via dispersion as toward the extraction wells while the extraction wells are being pumped. This does not seem reasonable or believable. Considering the significant uncertainty in the pilot test results, as documented by Dr. Pope in his May 17, 2016 memo, it is likely that dispersivity values determined from the same test are also highly uncertain. These figures do not provide confidence that the sulfate can be adequately distributed with the planned injection system."

AF replied: "The model simulates two primary steps in the addition and distribution of sulfate. In step 1, extraction pumping is simulated to pull injected sulfate into place. Step 1 pumping is stopped at the

approximate time that the sulfate reaches the extraction well and at that time step 2 begins. Step 2 relies on ambient flow, molecular diffusion, and dispersion to further distribute sulfate. Therefore, the particle tracking shows step 1, the advective flow lines between extraction and injection wells under imposed gradient. Once the pumping stops, the simulation shows the expected movement and redistribution of sulfate under the ambient flow regime, or step 2. The dispersivity constants that were used in the model were 20 feet in the longitudinal direction and 6.7 feet in the transverse direction. The transverse dispersivity constant is the most sensitive to lateral spreading of the sulfate, especially under ambient flow (step 2). The transverse dispersivity value was determined by analyzing the push-pull test: this analysis is included in RD/RAWP Addendum 2 (Appendix C). Considering published values for dispersivity in similar aquifers and at similar scales, the value of 6.7 feet is below the average at approximately 9.5 feet (Gelhar, 1992). Based on this rationale, once distributed as part of step 1, the sulfate will advect, diffuse, and disperse as simulated. As described, the analysis is based on the data collected from the site. A phased approach to EBR is proposed, in part, to allow for adjustments to be made in response to remediation system behaviors that differ from modeled approaches. Phase 1 field application will provide further confidence in the approach or indicate changes are needed to improve sulfate distribution."

From: Davis, Eva [mailto:Davis.Eva@epa.gov]
Sent: Monday, February 27, 2017 1:43 PM
To: Dan Pope; d'Almeida, Carolyn K.
Cc: Henning, Loren; Wayne Miller (Miller.Wayne@azdeq.gov)
Subject: RE: rough draft

Several thousand ppm – do you have copies of the figures from appendix E? their own projection is that large portions of the contaminated area would have sulfate concentrations greater than several thousand ppm for years – years - after the injection of the junk. They plan on injecting at 320,000 ppm.

Air Force may not want to implement this in a manner that it will fail, but AMEC doesn't care -

From: Dan Pope [mailto:DPope@css-inc.com]
Sent: Monday, February 27, 2017 1:35 PM
To: Davis, Eva <Davis.Eva@epa.gov>; d'Almeida, Carolyn K. <dAlmeida.Carolyn@epa.gov>
Cc: Henning, Loren <Henning.Loren@epa.gov>; Wayne Miller (Miller.Wayne@azdeq.gov) <Miller.Wayne@azdeq.gov>
Subject: RE: rough draft

It would likely take several thousand ppm sulfate to become really toxic to the bugs. It's complicated, though, because there are so many factors in play. Easy to demonstrate toxicity in the lab, but the field is much more complex.

Of course it's good to have some toxicity around the injection point, to help reduce fouling of the injection points by too much bug growth.

And there's always a balance between choosing high and low concentration reagents (sulfate) for injection. You want to end up with a certain range of reagent concentrations in the contaminated groundwater, obviously, but to do that the reagent concentration in the injectate has to be much higher than the final desired reagent concentration after the injectate mixes with groundwater. Too low a concentration of reagent in your injectate, and you're just replacing contaminated groundwater with your injectate.

But I don't think AF is going out of its way to do EBR in a way that would make it fail. Doubtless they are trying to do it on the cheap, but surely they want it to work.

From: Davis, Eva [mailto:Davis.Eva@epa.gov]
Sent: Monday, February 27, 2017 9:15 AM
To: Dan Pope; d'Almeida, Carolyn K.
Cc: Henning, Loren; Wayne Miller (Miller.Wayne@azdeq.gov)
Subject: RE: rough draft

At what concentration does sulfate become toxic to the bugs?

If we want to consider at all letting AF/Amec try this for a period of a couple years, I think we need to push for a whole different approach than what is contained in addendum #2. What is contained in addendum 2 is a very high injection concentration and no containment whatsoever, and a huge footprint -

From: Dan Pope [mailto:DPope@css-inc.com]
Sent: Monday, February 27, 2017 8:48 AM
To: Davis, Eva <Davis.Eva@epa.gov>; d'Almeida, Carolyn K. <dAlmeida.Carolyn@epa.gov>
Cc: Henning, Loren <Henning.Loren@epa.gov>; Wayne Miller (Miller.Wayne@azdeq.gov) <Miller.Wayne@azdeq.gov>
Subject: RE: rough draft

I should have summed that email up a bit better! It's very true, of course, that they should do what they can to provide steady sulfate concentrations over time, for optimization of EBR across the site. This would probably involve many more injection points and perhaps extraction points, which would be expensive and complicated to maintain (fouling, etc.), so I doubt if AF is going to be in favor of that. But overall, anything they are likely to agree to do to optimize sulfate concentrations across the site probably won't have that much overall long-term effect on remedy timeliness, because the overall timeliness thing is almost certainly controlled by COC movement from LNAPL to groundwater, rather than biodegradation rates of COCs in groundwater.

There is something to be said for limiting the geochemical footprint of the sulfate (water quality issues). But if they have good hydraulic control of site groundwater, that should suffice to control the footprint.

From: Davis, Eva [mailto:Davis.Eva@epa.gov]
Sent: Thursday, February 23, 2017 3:59 PM
To: Dan Pope; d'Almeida, Carolyn K.
Cc: Henning, Loren; Wayne Miller (Miller.Wayne@azdeq.gov)
Subject: RE: rough draft

I am aware of all of that – you have said that several times before.

Line 1044 of Addendum #2 states that they will inject TEA at a concentration of ~ 320 g/L and Figures in Appendix E of the document show that they plan on letting it disperse for more than 5 years. This is a far cry from some of the guidance on EBR by Suthersan et al., "**sulfate application strategies that employ repeat injections at highly elevated concentrations may not be as effective as sulfate delivery strategies that achieve relatively steady sulfate concentrations over time in the range of 100 to 2000 mg/L. This can increase the efficiency of the process while limiting the geochemical footprint of the reactions.**"

From: Dan Pope [mailto:DPope@css-inc.com]
Sent: Thursday, February 23, 2017 3:34 PM
To: Davis, Eva <Davis.Eva@epa.gov>; d'Almeida, Carolyn K. <dAlmeida.Carolyn@epa.gov>
Cc: Henning, Loren <Henning.Loren@epa.gov>; Wayne Miller (Miller.Wayne@azdeq.gov) <Miller.Wayne@azdeq.gov>
Subject: RE: rough draft

Eva:

The multiple batch injections of sulfate (as mentioned in *Draft_Final_ST012_RD-RAWP_Addendum2.pdf* Line 726: "Batch TEA injection will be performed in discrete phases separated by monitoring periods."), with recirculation to aid distribution, and monitoring is a useful approach. Whether that will allow EBR to be successful in any given timeframe depends on things we don't know much about, including LNAPL mass configuration in the subsurface.

Everything else being equal (good reagent distribution, appropriate geochemistry for sulfate reduction, useful populations of sulfate-reducers being developed, no significant salinity toxicity, no significant hydrogen sulfide toxicity, etc.), it would be expected that EBR would begin to control groundwater-dissolved COCs fairly soon, and to some degree the flux of COCs from LNAPL. What happens then is that COCs away from LNAPL masses can probably be fairly well controlled, especially with hydraulic control of the plume. This means that under good conditions, it would be expected that the COCs would be "chased back to the source LNAPL"; that is, the masses of LNAPL would be surrounded by envelopes of active microorganisms degrading COCs, reducing or even eliminating COCs beyond the envelope. This situation is what I expect, and what AF expects.

The problem is the **size and configuration** of the masses of LNAPL. **To simplify:** if the masses/smear zones/etc. are small (i.e., short COC diffusion paths from within the LNAPL to groundwater), with good groundwater flow (i.e., reagent distribution) all around the small masses of LNAPL, then depletion of COCs from the LNAPL is relatively fast. If the masses of LNAPL are large (i.e., long COC diffusion paths from within the LNAPL to groundwater), and/or groundwater flow around the masses is poor (poor reagent distribution) , then depletion of COCs from the LNAPL is relatively slow.

But we don't really know much about the LNAPL configuration, except that there is still a lot of LNAPL out there, and at least some of it is quite mobile (i.e., it moves into the wells), so at least some of the LNAPL is likely to be distributed in such a way that COC diffusion paths to groundwater are long, and also quite possibly groundwater and reagent distribution to the mass of LNAPL is poor.

AF is hoping that LNAPL mass configuration is such that COC diffusion pathways are short, and groundwater/reagent distribution around the LNAPL is good. I hope so too, but think that there are some masses of LNAPL out there that are not so happily distributed.

When some of the LNAPL is not well-distributed (from an EBR point of view), then after EBR proceeds for some time, as mentioned above, there will be some remaining masses of LNAPL, probably surrounded by an envelope of degraders, but still there. If performance monitoring samples are taken from a distance away from the LNAPL (perhaps a few months groundwater travel time, to pick a number), EBR may have been able to usefully reduce COC concentrations as found in those samples.

If, however, some of the performance monitoring samples are taken from in or very near the LNAPL mass, it is highly likely that COC concentrations will not meet RAOs in the short term.

So, EBR is very likely to end up with some degree of COC control in groundwater (at least away from the LNAPL masses), but with isolated pockets (which could be small, or large) of LNAPL that persist for some time. Regulators have to determine how important these isolated masses of LNAPL are, and how long they are willing to allow EBR/MNA to work to deplete those LNAPL masses.

From: Davis, Eva [mailto:Davis.Eva@epa.gov]
Sent: Thursday, February 23, 2017 2:10 PM
To: Dan Pope; d'Almeida, Carolyn K.
Cc: Henning, Loren; Wayne Miller (Miller.Wayne@azdeq.gov)
Subject: RE: rough draft

My edited version is attached – the letter I believe is real good, I'd just like to see it more strongly request the containment be initiated. I added a sentence to this effect. I think we need to discuss Dan's comments more - do you think that the way they are proposing to implement EBR in addendum #2 would be successful?

From: Dan Pope [mailto:DPope@css-inc.com]
Sent: Thursday, February 23, 2017 9:19 AM
To: d'Almeida, Carolyn K. <dAlmeida.Carolyn@epa.gov>; Davis, Eva <Davis.Eva@epa.gov>
Cc: Henning, Loren <Henning.Loren@epa.gov>; Wayne Miller (Miller.Wayne@azdeq.gov) <Miller.Wayne@azdeq.gov>
Subject: RE: rough draft

I've included a few comments and possible edits.

From: d'Almeida, Carolyn K. [mailto:dAlmeida.Carolyn@epa.gov]
Sent: Wednesday, February 22, 2017 3:33 PM
To: Davis, Eva; Dan Pope
Cc: Henning, Loren; Wayne Miller (Miller.Wayne@azdeq.gov)
Subject: rough draft

Yesterday, Loren asked us to put together a draft response to Phil's letter of February 10 stating AFs intent to move forward with EBR regardless of agency objections. Following the meeting of Feb 14, we agreed to provide AF a list of our information needs to get on board with the EBR proposal; we have another call scheduled for tomorrow at 11 to discuss. I have taken a stab at a draft response, don't consider it anywhere near complete or final but only what I can put together in a day, for discussion tomorrow. Please feel free to add to this draft.

Carolyn d'Almeida
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"Because a waste is a terrible thing to mind..."