From:	DeVenecia, Eric R - DNR
To:	David Beattie; Sager, John E - DNR
Cc:	Bill Snellman; Matthew Turner; Katie Wolohan
Subject:	RE: Superior Refinery - Revised Sampling and Analytical Plan 11/15/2018
Date:	Monday, November 19, 2018 9:16:33 AM

Dave
The changes to the treatment system monitoring you proposed in #1 and #2 below and the revised Sampling and Analytical Plan (updated 11/15/2018) are acceptable. All other conditions of the letters of coverage and general permit will continue to apply.

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From: David Beattie <David.Beattie@huskyenergy.com>
Sent: Friday, November 16, 2018 12:09 PM
To: DeVenecia, Eric R - DNR <Eric.DeVenecia@wisconsin.gov>; Sager, John E - DNR <John.Sager@wisconsin.gov>
Cc: Bill Snellman <Bill.Snellman@huskyenergy.com>; Matthew Turner <Matthew.Turner@huskyenergy.com>; Katie Wolohan <kwolohan@barr.com>
Subject: RE: Superior Refinery - Revised Sampling and Analytical Plan 11/15/2018

Eric –

The double results in the spreadsheet for 10/15 that you mentioned were a double typo.
The 2nd result should have been for 10/17 and the PFBA result should have been 110 instead of 100.

Here is an approximate timeline of the carbon changeouts/operation for our systems:
5/25 – System 1 in operation
7/5 – System 2 in operation, system 1 down for carbon changeout
9/7 – System 1 in operation, system 2 down for carbon changeout
9/15 – Both systems online
10/28 – Just system 2 in operation, system 1 down for carbon changeout
11/1 – Both systems online
11/5 – Just system 2 in operation (decreased flow to WWTP)

As for the PFBA and PFPeA partial breakthrough here is some information provided by the subject matter expert with BARR Engineering (Katie Wolohan) that we have been working with since the event:

PFBA and PFPeA are typically the first PFAS compounds to breakthrough in granular activated carbon

(GAC) systems or ion exchange (IX) systems; what we have observed is not unexpected or concerning. PFPeA has been at non-detectable concentrations at SP-6/SP2-6 (composite), the treatment system effluent since 10/24/2018. As of 11/12/2018, the concentration of PFBA at the treatment system effluent was 560 ppt – this is likely because of the following:

1. The lead GAC vessels have little to no adsorption capacity left for PFBA because these were formerly the lag vessels of each treatment system and had already exhibited PFBA breakthrough as lag vessels prior to being moved into the lead positions. So now the lag vessels, which have newer/virgin GAC, have to do the heavy lifting for all of the PFBA in the influent in general, plus what is being kicked off of the lead vessel (larger chain PFAS will kick off shorter chains, like PFBA and PFPeA on both GAC and IX resin, which is why at times we see higher concentrations of PFBA at SP-2/SP2-2 than at SP-0A/SP-0B.
2. As a result of item #1, PFBA has already broken through at SP-3/SP2-3, after the lag GAC vessels. This coupled with the fact that PFBA had already broken through IX previously results in the concentrations we are currently seeing. The IX resin has likely minimal to no adsorption capacity left for short chain compounds like PFBA and PFPeA.

There is not much else we can do to better remove PFBA short of adding more vessels in series of either GAC or IX, and the improvement would be marginal. Including ion exchange in the first place was our attempt at keeping shorter chain compounds out of the effluent as long as possible. PFBA and PFPeA are both short chain acids, only 4 and 5 carbon atoms respectively, and much more difficult to adsorb onto GAC and IX resin. In most treatment systems we have studied monitoring data for, and in the data provided by the water treatment vendors, PFBA is always the first to breakthrough and it usually happens much sooner than PFOS/PFOA (PFPeA is typically the second compound to breakthrough). PFBA and PFPeA are also competing with the long chain compounds at much higher concentrations for adsorption sites.

We do not consider breakthrough of PFBA or PFPeA, in general or at the concentrations we are currently seeing, an indication that treatment is not working as designed or that there is a risk of breakthrough of PFOA or PFOS. To date, we have not observed any breakthrough of PFOA or PFOS after the lag GAC vessel, which suggests that to date the resin has not likely seen PFOS or PFOA, or in the effluent (after IX) on either train of the treatment system. At this time we do not plan to changeout of the IX resin – it likely has sufficient adsorptive capacity remaining, especially for longer chain compounds that are of greater concern: PFOA and PFOS. We have established the following plan for changeout of the IX resin in coordination with Clean Harbor and Barr Engineering:

- **Resin changeout will be recommended when we see breakthrough at the composite effluent (at any concentration) of either perfluoroheptanoic acid (PFHpA) OR perfluorohexane sulfonate (PFHxS).**
    - These PFAS have 7 carbon atoms (PFHpA) and 6 carbon atoms (PFHxS) in their chains. PFOA and PFOS each have 8 carbon atoms in their chains.
    - It is expected that PFHpA will break through before PFHxS, given that resin has less adsorptive capacity for acids (the PFAS with "A" at the end) than for sulfonates (the PFAS with "S" at the end). PFHpA breakthrough would suggest PFOA may be the next acid to breakthrough, and breakthrough of PFHxS would suggest that PFOS may be the

next sulfonate to breakthrough.

- **We expect that breakthrough of PFHpA would precede breakthrough of PFOA and that breakthrough of PFHxS would precede breakthrough of PFOS, both with a reasonably conservative margin**. We expect to maintain non-detectable concentrations of PFOS and PFOA at the discharge with these change-out criteria.

Additionally, for reference, Minnesota has a health risk limit (HRL) of 7.0 ug/L for PFBA for drinking water, or 7,000 ng/L. A health risk limit is the concentration of a contaminant, or a mixture of contaminants, that can be consumed with little or no risk to health and which has been promulgated under rule. While we are technically observing breakthrough of PFBA in the effluent of the treatment system, the concentration is well below the drinking water HRL in Minnesota (Wisconsin does not have a health risk limit or guidance value for PFBA), as in the treated water is of an acceptable quality for human consumption as it pertains to PFBA per the state of Minnesota.

Hopefully this is all helpful.

Thanks,
Dave

From: DeVenecia, Eric R - DNR [mailto:Eric.DeVenecia@wisconsin.gov]
Sent: Friday, November 16, 2018 10:48 AM
To: David Beattie <David.Beattie@huskyenergy.com>; Sager, John E - DNR <John.Sager@wisconsin.gov>
Subject: RE: Superior Refinery - Revised Sampling and Analytical Plan 11/15/2018

Thanks Dave, I had noticed that language and understood what you were trying to convey (the Merit method was available from a footnote on the table) but thanks for confirming.

The next question is re the analytes that are showing breakthrough in the effluent - PFBA and PFPeA. Please provide some comments re what will be/is being done to address the partial breakthrough issue. When those parameters show up, how long until PFOA/PFAS break through?

Eric

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From: David Beattie <David.Beattie@huskyenergy.com>

Sent: Friday, November 16, 2018 10:19 AM
To: DeVenecia, Eric R - DNR <Eric.DeVenecia@wisconsin.gov>; Sager, John E - DNR <John.Sager@wisconsin.gov>
Subject: RE: Superior Refinery - Revised Sampling and Analytical Plan 11/15/2018

Eric/John,

Looks like something happened with putting together the language for the email I sent below.

The last paragraph should have read:

We are also keeping our options open with our analytical labs. We have been using Merit, which uses a modified D7979, but there is a possibility of us using Maxxam Analytics, which uses modified EPA method 537. We have analysed several split samples between laboratories and are confident that switching labs will not bias the monitoring data if indeed we switch.

Sorry!
I'll get you the other information shortly.

Dave

From: DeVenecia, Eric R - DNR [mailto:Eric.DeVenecia@wisconsin.gov]
Sent: Friday, November 16, 2018 9:38 AM
To: David Beattie <David.Beattie@huskyenergy.com>
Subject: RE: Superior Refinery - Revised Sampling and Analytical Plan 11/15/2018

Thanks Dave,
I will forward to our central office and discuss with them ASAP.

Question on the data you sent me on 10/26. The last two columns of the table for SP-6/SP2-6 Composite includes two normal (N) samples, both collected on 10/15. Is that correct?
Also, can you provide the dates that carbon was switched out?

Thanks

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From: David Beattie <David.Beattie@huskyenergy.com>
Sent: Thursday, November 15, 2018 4:40 PM

To: Sager, John E - DNR <John.Sager@wisconsin.gov>; DeVenecia, Eric R - DNR <Eric.DeVenecia@wisconsin.gov>
Cc: Matthew Turner <Matthew.Turner@huskyenergy.com>; Bill Snellman <Bill.Snellman@huskyenergy.com>; Katie Wolohan <kwolohan@barr.com>
Subject: Superior Refinery - Revised Sampling and Analytical Plan 11/15/2018

John/Eric,

We would like to request the changes outlined below to our sampling and analytical plan. We have been operating the PFAS water treatment systems for 6 months, and we have a better understanding of when 50% breakthrough will occur after the lead granular activated carbon vessels. Sampling and analytical plans that reflect the requested changes are attached to this email

1. **Decrease treatment system monitoring of PFAS** at all sampling ports to one time per week rather than two times per week.
2. **Decrease our treatment system monitoring of general chemistry parameters** to monthly rather than weekly. We would also like to **reduce the number of sampling locations** to just the influent and effluent of the treatment system rather than at every sampling port. Since operating the treatment system we have not observed severe imbalances in the ions monitored.
3. **Decrease our off-site PFAS monitoring at 3rd St., 21st St, and at the mouth of Newton Creek** to monthly rather than biweekly. Over the winter we intend to recirculate treated water at times rather than discharging. This will help maintain sufficient water onsite to keep the WWTP running. This sampling is for informational purposes only and we feel reducing this sampling does not directly impact decision making in regards to the site and recovery activities. Depending on ice and lack of flow, this sampling may or may not be possible at times.

We are also keeping our options open with our analytical labs. We have been using Merit, which uses a modified switch analytical laboratories for PFAS monitoring from Merit to Maxaam Analytics, which uses modified EPA method 537. We have analysed several split samples between laboratories and are confident that switching labs will not bias the monitoring data.

Please let us know if WDNR accepts these changes or if you have any questions. **We would like to implement these changes beginning 11/19**.

If you would like to have a call to discuss after you have had a chance to look over please let me know.

Thanks,
Dave

David Beattie
Senior Environmental Technologist

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