Uinta Basin Produced Water Emissions Inventory Development: Conference Call Notes and Further Discussion

Call date: September 20, 2017

Utah Division of Air Quality (DAQ); USU Bingham Entrepreneurship & Energy Research Center (USU)

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Objectives of call:

- Discuss methods for estimating emissions from produced water ponds by combining methods used by DAQ with research and analysis done by USU
- Use the results of this discussion to facilitate agreement on an approach for a "Phase I" produced water emissions inventory
- Gather consensus among all stakeholders during the planned October 5, 2017 conference call for a complete 2014 Air Agencies oil and gas emissions inventory

Inventory Structure

DAQ suggested that it is important to distinguish between an inventory developed by a regulatory agency and those that are developed for research purposes since each have different sets of constraints. In general, regulatory inventories combine "activity factors" with "emission factors" so that a change in activity from year to year can be accounted for in an annual inventory. DAQ stated that the detailed comments and questions provided by USU before the call helped to clarify an approach that could be used to resolve disagreements. In DAQ's view, if agreement could be found on how the inventory is structured, focus could be placed uncertainty in emission factors.

Since the Utah Division of Oil Gas and Mining requires pond operators to report the amount of liquid throughput to the ponds, this annual "activity" is easily accessible to DAQ. This data was used as the basis for DAQ's pond inventory estimates. USU agreed that an inventory approach that uses throughput and along with VOC speciation of the water coming into the ponds seems like a reasonable method to create an inventory of "actual" emissions on a year to year basis.

Emission Factors

The greater uncertainty lies in the emission factor calculation. Both DAQ and USU agreed that more research, analysis and insight are required to figure this out. USU's research has pointed to the myriad

sources of uncertainty in potential carbon sinks that would affect a mass-balance calculation which assumes that all of the VOC that enters a facility is evaporated to the air. Some of the potential sinks include:

- Oil that is skimmed off ponds and sold
- Sludge collected on the bottom of skim ponds
- Hydrocarbons that are decomposed by bacteria into CO2
- Decomposition of heavy, involatile hydrocarbons into more volatile compounds
- Strong stratification in ponds could lead to organics that remain in ponds for a very long time (possibly years) because they don't have opportunity to interact with the surface

Sampling

Routine sampling of hydrocarbons in water is usually limited to gasoline-range organics (GRO), diesel-range organics (DRO), and benzene, toluene, ethylbenzene, and xylene (BTEX). GRO measures organics in approximately the C6-C10 range, while DRO measures organics between roughly C10 and C28. USU has developed a method for speciated measurements of C1-C11 hydrocarbons in produced water, but the method has high uncertainty for some compounds.

Methods to measure hydrocarbons larger than C11 or C12 in ambient air are different than methods for C1-C12 hydrocarbons because heavy hydrocarbons are only semi-volatile. Hydrocarbons larger than C12 are rarely measured in ambient air because their concentrations are low. USU's measurements of the composition of and emissions from produced water in the Uintah Basin only considered C1-C11 hydrocarbons and C1-C3 alcohols (in Wyoming they also measured carbonyls).

DAQ has found that the majority of hydrocarbons in produced water are DRO, but USU has not measured most DRO-range compounds in water or emissions. DRO compounds may degrade into smaller, more volatile compounds, which could be oxygenated organics or hydrocarbons. In DAQ's sampling studies, samples were collected from five facilities in December (2016). Averages of these measurements were used. Four of these facilities were no longer using skim ponds, so only measurements from one facility could be used from estimating emissions from skim ponds. A 50% degradation factor was assigned to DRO measurements, meaning that it was assumed that 50% of DRO was emitted to the atmosphere as VOC, while 50% remained in the pond or was emitted as CO_2. Research is needed to understand the fate of DRO in produced water ponds.

DAQ used water that was sampled before entering ponds. Some of the oil in this water floats to the top in skim ponds and is removed and sold. Estimating this would be very difficult as this number is not required to be reported.

USU's measurements show that water tends to be richer in hydrocarbons in winter relative to summer. Anecdotal reports from industry are that more oil exists in produced water during winter, and more is skimmed off during winter and sold. Much of the surface of produced water ponds is frozen over in the winter, and ice cover effectively stops all emissions. The result of these two competing phenomena is that emissions from produced water ponds tend to be similar in summer and winter.

In some cases USU's and DAQ's Basin-wide emissions estimates compared well, while in other cases they did not. For example, DAQ calculated 1300 U.S. tons of VOC emitted from evaporative ponds (DAQ's estimates did not include methanol), while USU estimate for hydrocarbons (excluding alcohols) is 926 U.S. tons per year (they have 95% confidence the number lies between 553 and 1610 tons) . These measurements are within the same order of magnitude, and the uncertainties of these calculations also make these comparable. Skim ponds, however, show a greater discrepancy. DAQ calculated 71,461 tons per year, while USU estimated (excluding alcohols) 1538 tons per year (they have 95% confidence the number lies between 298 and 5982 tons).

It is likely that much of this discrepancy likely lies in the difficulty to specify carbon sinks, as discussed above. For skim ponds in particular, much of the hydrocarbons assumed to emit to the atmosphere in DAQ's estimates may be removed as oil skimmed from the pond surface. In the near future DAQ intends to make a request for data from three produced water facilities. This will provide 15 more data points with sample information. As more data continues to be gathered it can be used in future versions of produced water inventories. Skim ponds tend to be covered ⅓ to ½ in a frothy layer of oil. When making measurements over oil vs. nearby water, hydrocarbon emissions tend to be 10-30x higher over oil. The variable extent of oil cover on skim ponds led to a large confidence interval in USU's skim pond emissions estimate.

USU estimated that alcohol emissions (mostly methanol) account for 69.8% of total non-methane organic compound emissions (they have 95% confidence the number lies between 62.8 and 76.5%), while DAQ did not estimate alcohol emissions.

DAQ's VOC emissions estimate is not speciated. USU's emissions measurement dataset provides the only measurement of the VOC speciation of produced water pond emissions that has ever been collected, and it can be used to speciate the estimated emissions. Uncertainty exists about how to apply USU's emission speciation to DAQ's emissions estimates, since USU measured emissions mainly in the GRO range, while DAQ's estimate includes a large fraction of DRO in water. As discussed above, it is not clear how (or if) DRO decomposes to GRO-range compounds, which are then emitted, or if some fraction of DRO compounds are directly emitted.

Conclusions + Future Work

Both USU and DAQ agree that DAQ's emissions from skim ponds are likely over-estimated. As pointed out above, the calculations among the two methods for what DAQ calls evaporation ponds are actually quite close. This suggests that the most fruitful direction for the near-term, Phase I product is to agree on a correction factor for the skim pond emission factor for the 2014 air agencies inventory. To establish this factor a wider group of participants beyond DAQ and USU, drawn from the inventory stakeholder group, would be desirable.

It would be useful to measure how the composition of produced water, as well as the composition of emissions from produced water, change over time. It would be most useful to make speciated (or at

least speciated by carbon number) measurements for the range of GRO through DRO (C6-C28). This would provide information about the speciation of GRO and DRO in water, how (and whether) DRO decomposes to smaller compounds, and whether those compounds get emit into the atmosphere. This will help inform estimates of emissions made from DRO and GRO measurements in water.

EPA's Water9 model could also be used as a research tool to evaluate emissions estimates. There are a number of areas of uncertainty in this model as it was not designed specifically to be used for produced water facilities.