ARE PRODUCED WATER EMISSION FACTORS ACCURATE?

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Abstract

Rules of thumb are often used for estimating emissions from Produced Water storage tanks, especially when entrained hydrocarbons are present. The rules of thumb are used because of difficulties in obtaining accurate compositional information as well as deficiencies in the estimation calculation methods. The different rules of thumb yield substantially different emissions estimates, and it is questionable whether some provide accurate estimates. A new process simulator-based method is presented that overcomes some of the sample analysis and calculation shortcomings. Predictions of the new method are presented that show the effect of hydrocarbon entrainment on produced water emissions. In addition, definitions and emissions estimates of some of the currently used rules of thumb are presented and contrasted with the new method.

Introduction

Rules of thumb are often required to estimate hydrocarbon emissions from produced water storage tanks due to lack of sampling or inadequacies of sample analysis, the "1% rule" being the most common. The premise behind the 1% rule is that entrainment from upstream separation introduces hydrocarbon liquids into the produced water tank. This entrained material forms a layer of hydrocarbons that float on top of the water in the tank and should be expected to increase total emissions. As it is difficult to measure the entrained oil content in the water fed to the tank, there is uncertainty in how much of this entrained oil is lost to emissions. The 1% rule is therefore applied as an estimate.

If 1% entrainment is assumed, a problem arises as to how this should be incorporated into typical emissions calculations. In discussions with industry colleagues, this author has found at least four different definitions for the 1% rule and how it should be applied. As each method produces significantly different estimates, the question then arises, do any of these methods provide accurate estimates of produced water tank emissions? Which of these methods makes the most sense?

Storage tank emissions are commonly divided into four categories; flashing, working, breathing, and loading. Flashing losses occur from vaporization of components in the tank inlet due to a pressure decrease and/or temperature increase of the material. These losses occur when the material is introduced to the tank. Working, Breathing, and Loading Losses (WB&L) occur as the material in the tank weathers or as it is removed. They are all caused by a changing vapor space in the tank. For working losses, this is by liquid level changes in the tank. Working losses increase as tank throughput and hydrocarbon vapor pressure increase. Breathing losses are the result of daily ambient temperature changes as the changing temperature causes the vapor space in the tank to expand and contract. Breathing losses increase with vapor pressure and are not directly influenced by tank throughput. Loading losses occur as vapors in a cargo transport vessel are displaced by liquid being loaded into the vessel. These losses increase as tank throughput and vapor pressure increase.

Before evaluating the various methods of applying the 1% rule, it makes sense to discuss a few items. How do hydrocarbons make their way to the produced water storage tank? Is there a logical method that would provide a more rigorous estimate of emissions than methods currently employed?

A diagram of a typical well site configuration can be seen in Figure 1. After exiting the well head choke, the well stream is commonly a three-phase mixture of gas, hydrocarbon liquid, and aqueous liquid. The gas is first separated from the liquid mixture in a high-pressure separator (HPS). After leaving the HPS, liquids will then flow to a heater treater (HT), where more gas is removed, and the two liquid phases are separated at an elevated temperature and reduced pressure (typically 20 to 50 psig). The produced water leaving the HT then flows to the Produced Water Storage Tank, and the hydrocarbon stream to the Hydrocarbon Storage Tank where they are stored until loaded and transported away from the wellsite.
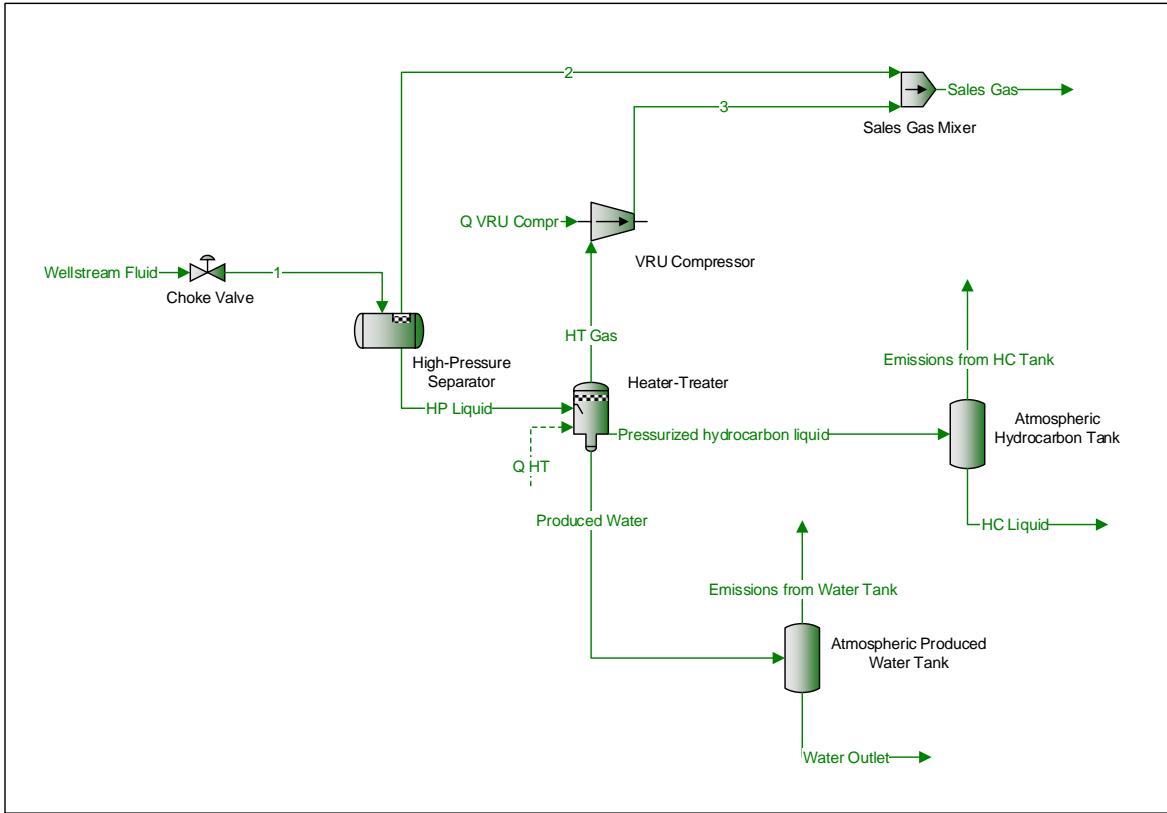
Figure 1: Typical well-site configuration

Hydrocarbons can make their way to the produced water storage tank in two ways, either by dissolving in the water or by mechanical carry under known as entrainment. While it is often said "oil and water don't mix", hydrocarbons are in fact slightly soluble in water, with lighter hydrocarbons and aromatic components being the most soluble. This solubility increases somewhat proportionally with pressure, and it is dependent on the concentration of salts in the produced water. The solubility is highest in pure water and declines with increasing salt concentration. An estimation of dissolved hydrocarbons on a "salt-free" basis would produce a conservative estimate if using a process simulator. There are also analytical techniques that mimic the pressure reduction from upstream separator conditions to storage conditions, providing an additional estimate of the flashing emissions from dissolved hydrocarbons in the produced water.

The results of these estimation techniques will confirm the expected low solubility of hydrocarbons in the water, and therefore a low contribution of overall emissions by the dissolved hydrocarbons. Table 1 gives the separator conditions and compositions for four samples of pressurized liquids leaving HTs. For Sample 1, the equilibrium dissolved hydrocarbon solubility in pure water predicted by ProMax® [1] is below 100 ppm, indicating a low contribution to overall emissions from dissolved hydrocarbons.

The second way that hydrocarbons enter the produced water storage tank is as an entrained second phase, and this second phase is a significantly greater contributor to emissions than the

2

dissolved hydrocarbons. To estimate emissions from the entrained liquid, the composition and volume of the material must be known. The entrained hydrocarbon droplets are the same material as the hydrocarbon liquid stream leaving the HT, a material of which the composition is typically known. However, what is usually unknown is the size or total volume of the droplets that are entrained.

Separators are designed to remove droplets of a certain diameter and larger. Typical minimum droplet diameters are in the 100- to 150-micron range. A fraction of the droplets smaller than this threshold will be entrained due to inadequate residence time in the separator. Directly measuring these droplets, either in terms of size or total volume, is difficult. The amount of entrainment is therefore typically assumed or estimated. Some individuals assume 200 ppm hydrocarbon leaving the HT with the produced water. A separator manufacturer questioned for this paper stated their typical design point is 0.5% (5000 ppm). Meanwhile, companies reclaiming hydrocarbons from produced water estimate 1 to 2% of the material entering the tank is entrained hydrocarbons.

With such widely varying estimates of entrainment and no reliable or cost effective way to measure the hydrocarbon content, it is helpful to look for alternative ways to estimate entrainment. Fortunately, one can look at what is *leaving* the tank to estimate what is *entering*. As the produced water with the entrained hydrocarbon droplets enters the storage tank, a portion of the hydrocarbons will flash due to the lower pressure and enter the vapor space. The remaining liquid hydrocarbons will eventually coalesce as a separate layer on top of the water. Care is taken to avoid removing material from the hydrocarbon layer when unloading the water. The hydrocarbon layer itself is removed periodically by the operator in known quantities. As the hydrocarbon layer is only removed intentionally, the rate at which entrained hydrocarbons enter the tank can be estimated by monitoring the rate at which they are removed.

Table 1: Sample conditions and compositions of hydrocarbon mixtures from wellsite facilities

Sample	1	2		3	4
Temperature, °F	120	66		146	130
Pressure, psia	56.7	56.7		45.7	29.7
Composition, mol%					
Methane	0.41%	0.89%	H2S	0.00%	0.00%
Ethane	2.07%	2.56%	N2	0.01%	0.01%
Propane	5.12%	5.45%	CO2	0.03%	0.01%
i-Butane	1.31%	1.33%	Methane	0.15%	0.05%
n-Butane	6.17%	6.22%	Ethane	1.18%	0.61%
Isopentane	2.32%	2.30%	Propane	4.69%	3.68%
n-Pentane	4.19%	4.15%	i-Butane	1.11%	0.96%
2-Methylpentane	2.20%	2.17%	n-Butane	5.51%	5.26%
n-Hexane	2.30%	2.26%	2,2-Dimethylpropane	0.12%	0.03%
2,2,4-Trimethylpentane	0.12%	0.12%	i-Pentane	2.64%	2.57%
n-Heptane	10.21%	10.05%	n-Pentane	3.75%	3.46%
n-Octane	9.08%	8.93%	2,2-Dimethylbutane	0.02%	0.02%
n-Nonane	3.78%	3.71%	Cyclopentane	0.00%	0.00%
Benzene	0.28%	0.28%	2,3-Dimethylbutane	0.63%	0.52%
Toluene	0.93%	0.92%	2-Methylpentane	1.61%	1.44%
Ethylbenzene	0.34%	0.33%	3-Methylpentane	1.00%	0.89%
p-Xylene	1.44%	1.41%	n-Hexane	2.64%	2.25%
C10+	47.72%	46.90%	Methylcyclopentane	2.37%	2.15%
			Benzene	0.24%	0.24%
Note: C10+			Cyclohexane	1.36%	1.18%
Molecular Weight = 282.7			2-Methylhexane	0.93%	0.81%
Specific Gravity = 0.88			3-Methylhexane	0.86%	0.78%
			2,2,4-Trimethylpentane	0.00%	0.00%
			2-4-Dimethylpentane	2.80%	2.54%
			n-Heptane	2.06%	1.76%
			Methylcyclohexane	2.97%	2.56%
			Toluene	0.81%	0.69%
			2,3,3-Trimethylpentane	5.65%	5.11%
			n-Octane	1.80%	1.57%
			Ethylbenzene	0.91%	0.17%
			m-Xylene	0.79%	0.56%
			o-Xylene	0.40%	0.51%
			Hexane, 2,3,4-Trimethyl-	5.49%	4.58%
			n-Nonane	1.50%	1.17%
			2-Methylnonane	5.12%	4.65%
			n-Decane	1.04%	0.94%
			Nonane, 2,3-Dimethyl-	5.05%	4.46%
			C12	3.82%	3.73%
			C13	3.81%	3.93%
			C14	3.18%	3.26%
			C15	2.44%	2.76%
			C16	1.95%	2.46%
			C17	1.65%	1.99%
			C18	1.53%	1.86%
			C19	1.45%	1.91%
			C20	1.03%	1.39%
			C21	0.87%	1.39%
			C22	0.86%	1.28%
			C23	0.69%	1.18%
			C24	0.59%	1.13%
			C25	0.62%	1.03%
			C26	0.39%	0.72%
			C27	0.43%	0.92%
			C28	0.35%	0.80%
			C29	0.29%	0.76%
			C30	6.82%	9.28%

AP 42 correlations for estimating WB&L

The Environmental Protection Agency (EPA) has recommended that Chapter 7 of AP 42 [2] be followed for estimating tank WB&L emissions for *organic liquid* storage vessels. The rules of thumb discussed in this paper all rely on AP 42 in some manner.

There are two basic components of the AP 42 methodology, Conditions and Throughput (C&T) and Vapor Pressure (VP). The C&T component is a set of equations for estimating emissions based on tank geometry, tank throughput, daily temperature changes in the vapor headspace, and hydrocarbon vapor pressure at the liquid surface.

For estimating vapor pressures of pure components, AP 42 recommends Antoine's equation and provides Antoine's coefficients for a number of organic liquids, although many of the common oil and gas components are not included. AP 42 also includes nomographs and equations for estimating vapor pressure of crude oil and refined petroleum stocks as a function of Reid Vapor Pressure and temperature.

For the vapor pressure of a mixture of components, AP 42 states that the *total vapor pressure* is simply the sum of the individual component partial pressures. AP 42 recommends that Raoult's law be used to calculate individual component partial pressures for hydrocarbon-only mixtures. Raoult's law states that the individual component partial pressure, p_i, can be calculated as

$$p_i = x_i P_i$$

where, x_i and P_i are the mole fraction and pure component partial pressure for component i, respectively. For *hydrocarbon mixtures* encountered in the oil and gas industry, the Raoult's law assumption is typically not problematic and will result in reasonable vapor pressure estimations. The EPA recently compared emissions data from organic liquid storage tanks versus estimates provided by AP 42 methods and found the predictions satisfactory [3]. Thus, it appears that the C&T component of AP 42 is sound *when teamed with reasonably good vapor pressure estimates*. This validates the C&T portion of the method in general.

If 1% entrainment is assumed, then the overall liquid would be 99 parts water and 1 part of the hydrocarbon. This would no longer be considered an organic liquid, and the application of Raoult's law would be problematic. Raoult's law applied to this mixture will greatly underestimate the vapor pressure and lead to severe underprediction of emissions.

For dilute aqueous solutions of hydrocarbons, AP 42 specifies that Henry's law be used to calculate hydrocarbon partial pressures. However, if a second liquid phase is present, using Henry's law can be problematic. Henry's law extrapolates the volatility of a component at *infinite dilution* which can lead to significant error (higher volatility than actual) when the hydrocarbon content is high enough to form a second phase. Further, the use of Henry's law requires knowing the Henry's constant for each component at the temperature of interest. AP 42 does provide Henry's constants at a single temperature, 25 °C, for a number of organic components in water. However, as with Antoine's coefficients, many of the common oil and gas components are not included.

When a hydrocarbon layer floats on top of an aqueous layer, the hydrocarbon vapor pressure is dependent on the temperature and composition of the hydrocarbon layer alone. The thickness of the layer is inconsequential. The practical effect of this is that WB&L losses will not vary linearly with the amount of hydrocarbon entering the tank. However, the hydrocarbon layer's composition in the tank does change over time due to depletion of the lighter components (i.e. heavy components remain while light components are removed as emissions). As the entrained fraction decreases, the hydrocarbon losses consume a larger fraction of the lighter components entering the tank. The net result is that the composition of the hydrocarbon layer may not be the same as the hydrocarbons entering the tank and in fact may be heavier. This reduces the hydrocarbon layer vapor pressure, leading to decreased emissions.

This paper will introduce a method that uses a process simulator to better estimate the vapor pressure of the floating hydrocarbon layer and take into account the depletion of lighter components from that layer. It will then present and compare produced water tank emissions estimates for various definitions of the "1 % rule".

A better way to estimate produced water emissions

Modern process simulators can provide accurate estimates of vapor pressure for hydrocarbon/water mixtures over a wide range of compositions and temperatures regardless of the number of phases present. It is logical therefore to replace Raoult's law or Antoine's estimates of the vapor pressure with those from the simulator, while using the C&T component of AP 42 to estimate emissions.

A tool was developed within ProMax to automate the use of the AP 42 C&T equations with ProMax hydrocarbon-water vapor pressure predictions. For brevity, this new tool will be referred to as the Proposed Produced Water (PPW) method.

The AP 42 C&T equations assume the use of a constant composition. The composition that is typically used is the incoming feed composition, with possibly some conditioning to account for the initial flashing of the feed as it enters the tank. The AP 42 methodology was originally developed for *hydrocarbon storage tanks* where the amount of material lost to emissions is very small compared to the throughput of material in the tank. The overall composition in the tank is assumed to be similar to the composition of the material entering the tank.

In *produced water tanks*, only a small fraction of the incoming feed is hydrocarbon. Since the hydrocarbon emissions do not change proportionally to the amount of incoming hydrocarbons, the hydrocarbons in the tank can become significantly depleted of the more volatile components when the entrainment is low. As the AP 42 equations are typically based on the incoming composition, *the predicted emissions of the lighter components can be greater than the feed rate of those components into the tank*.

In order to avoid this unrealistic result, one could develop a set of equations that attempts to determine the steady-state concentration of each component in the storage tank. However, for the sake of simplicity and clarity, the tool used here bases individual component emissions rates on the vapor pressure calculated from the incoming composition, capping the emissions for a given

component at that component's inlet rate (i.e. assuring that more of a component is not leaving a tank than entering). This should give conservative but reasonable WB&L estimates.

The ProMax PPW tool uses water that has been saturated with the known pressurized liquid composition at the temperature and pressure of the HT. This ensures that a reasonably conservative estimate of dissolved hydrocarbon emission is attained, and prevents solubilizing more hydrocarbons when the entrained hydrocarbons are added. The entrained pressurized liquid is used in the appropriate amount based on assumed entrainment, and the speciated emissions are predicted using AP 42 C&T correlations with ProMax vapor pressure predictions. The speciated emissions are capped at the incoming species flowrate.

PPW method predictions

Emissions estimations with the PPW methodology for a 500-bbl tank (vertical, fixed roof) were made and discussed below. Some AP 42 parameters that were used are shown in Table 2.

Table 2. AP 42-required parameters used in this comparison

Working and breathing parameters			
Tank geometry	Vertical cylinder	Max. avg. temp., °F	75.9
Tank height, ft	25	Min. avg. temp., °F	53.9
Tank diameter, ft	12	Avg. ambient press., psia	14.66
Number of tanks	1	Daily solar insolation, Btu/(ft^2-day)	1,388
Throughput, bbl/d	100	Tank and roof color	Medium Gray
Maximum fill	90%	Roof type	Cone
Average fill	50%	Roof slope (rise/run)	0.05
Loading loss parameters			
Land-based mode of operation	Submerged loading of a clean cargo tank		
Overall reduction efficiency	70%		

Using the information in the above table, WB&L emissions were estimated for the four representative samples. Figure 2 shows how the total emission estimates for the four samples are affected by the difference in composition of incoming hydrocarbons and the composition of the layer in the tank that has been depleted of lighter components. In the case of 1% entrainment, neglecting to account for component depletion would yield a threefold higher emissions estimate.
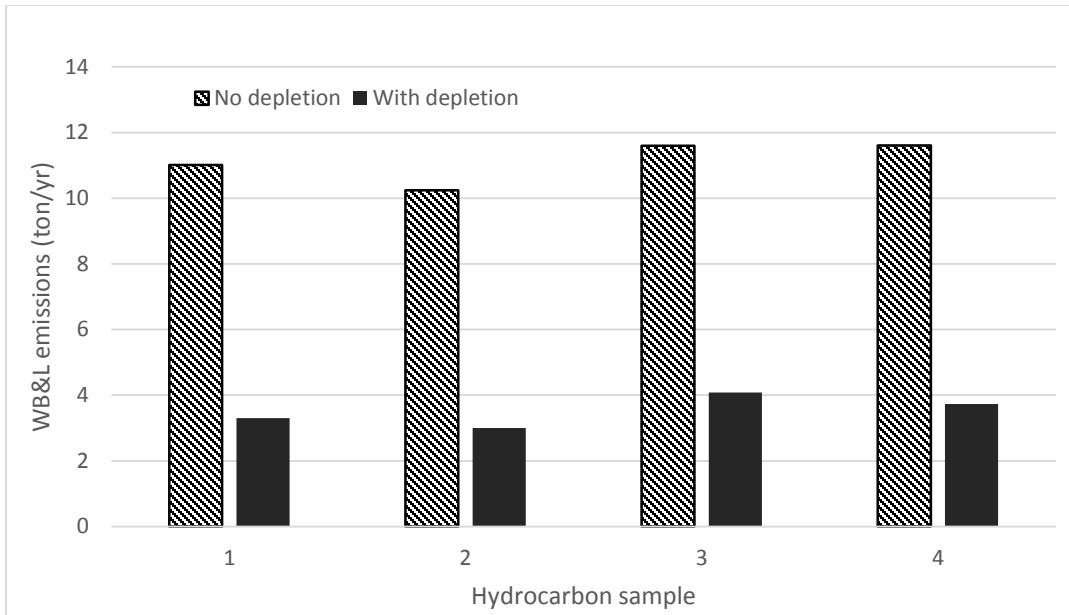
Figure 2: Comparison of estimated emissions rates when depletion of material in the tank is considered, assuming 1% entrainment.

The depletion of lighter components does not just affect the composition of the layer in the tank, it also effects the volume of hydrocarbon remaining in the tank. Since the composition of this layer has changed due to material being removed, depletion should be considered when estimating entrainment rates from the amount of hydrocarbon removed from the tank. Figure 3 shows that there is actually a noticeable loss of hydrocarbons due to depletion, especially at lower entrainment fractions. This should be considered when estimating incoming flow based on outgoing flow.
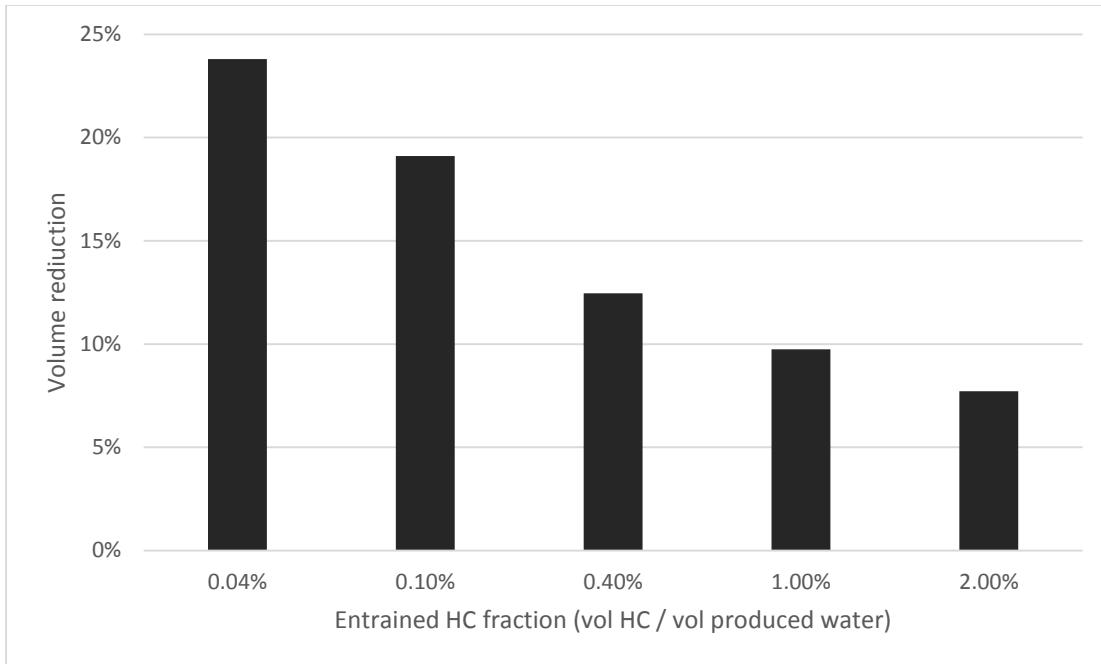
Figure 3: Reduction in total hydrocarbons remaining in the produced water tank when considering depletion due to vapor emissions.

Figure 4 (a-d) shows the Flash and WB&L predictions of this PPW methodology for each of the samples. It can be seen that the Flash emissions increase linearly with entrained hydrocarbon fraction, while the WB&L emissions increase rapidly and then begin to level off. For these four samples, the WB&L emissions at 1% entrainment averaged *one quarter* of the WB&L emissions of a tank with a pure hydrocarbon feed, even though the hydrocarbon flow is 100 times lower. Likewise, emissions estimated for 0.1% entrainment are around *one tenth* the emissions of a similar, pure hydrocarbon feed, even though the hydrocarbon flow into the tank is 1000 times lower.
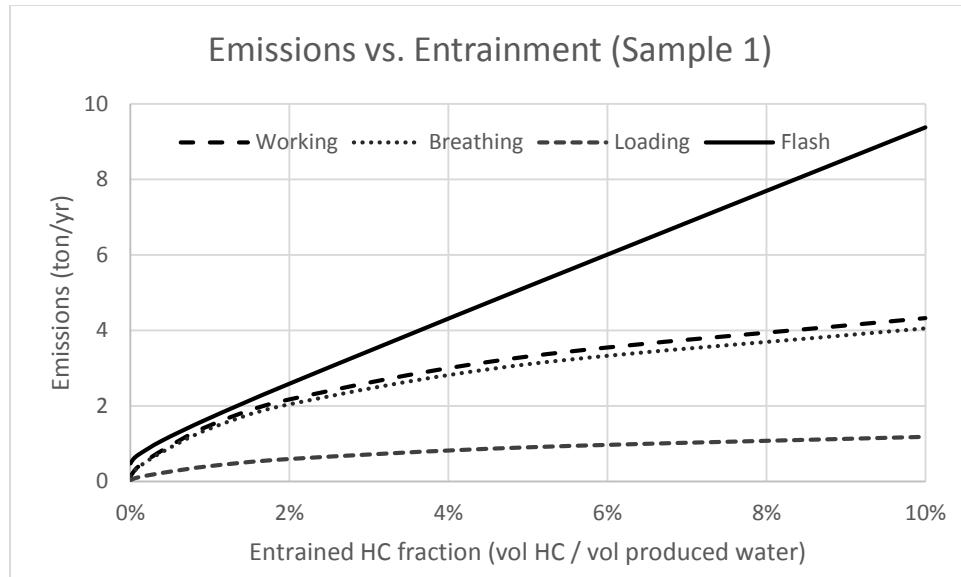
**Figure 4a:** Sample 1 emissions vs. entrained HC fraction
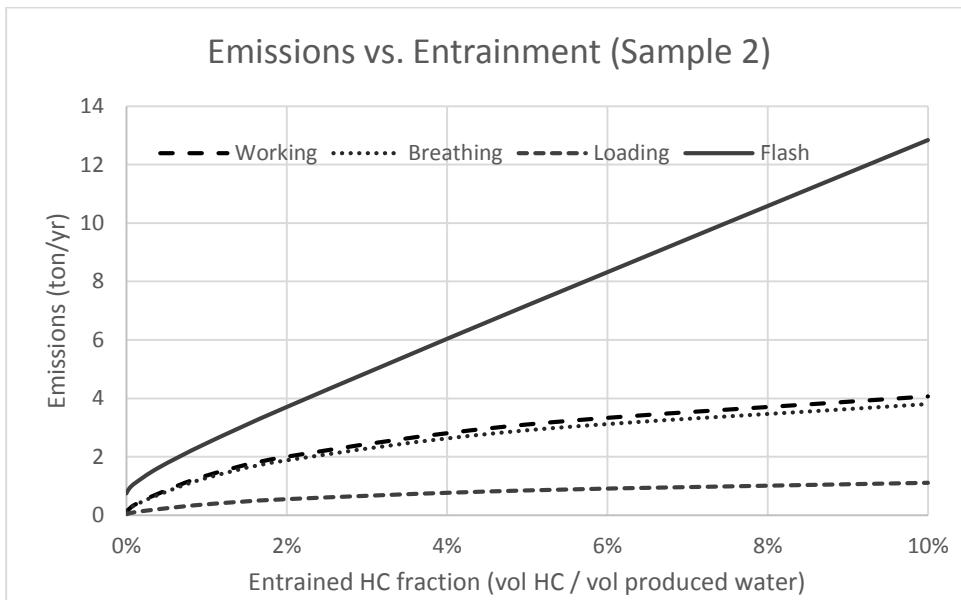
Figure 4b: Sample 2 emissions vs. entrained HC fraction
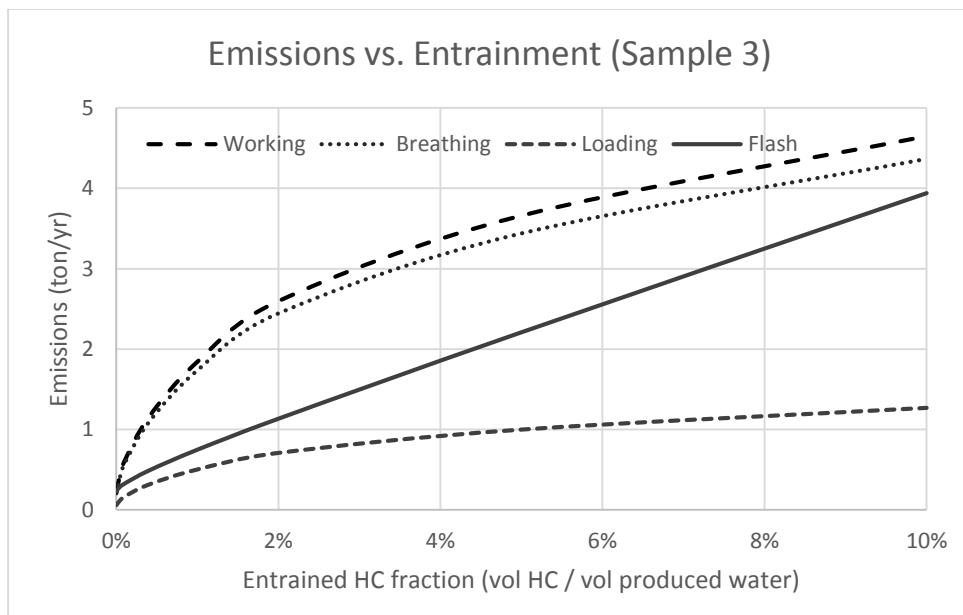
Figure 4c: Sample 3 emissions vs. entrained HC fraction
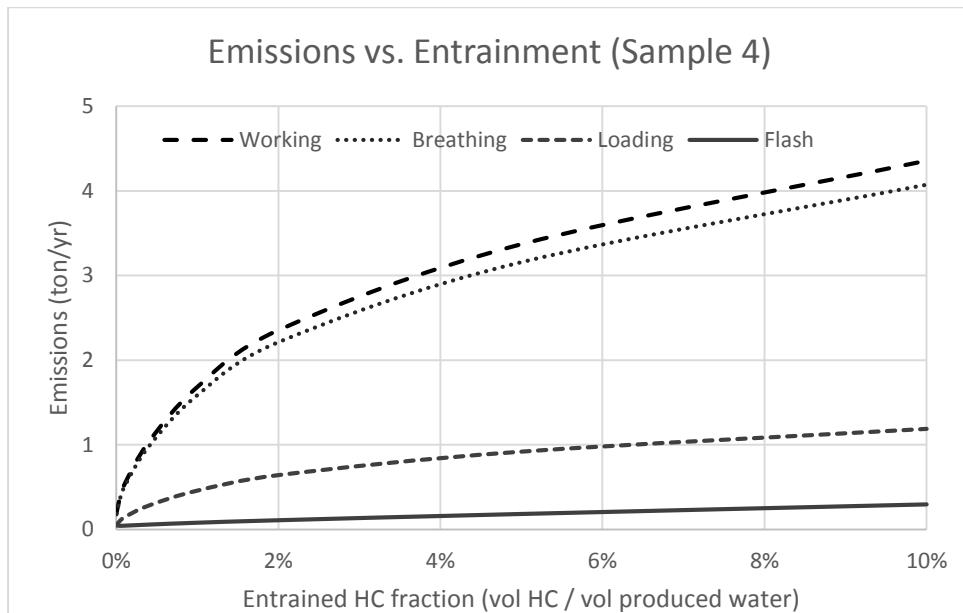

Figure 4d: Sample 4 emissions vs. entrained HC fraction

Figure 4e shows the same information as Figure 4a, but at very low entrainment fractions. It can be seen that when entrainment is assumed to be zero, the emissions are not zero. This is due to the dissolved hydrocarbons in the water. As mentioned previously, the estimates used here represent emissions from hydrocarbons in salt-free water, which should be an upper bound on actual dissolved emissions.
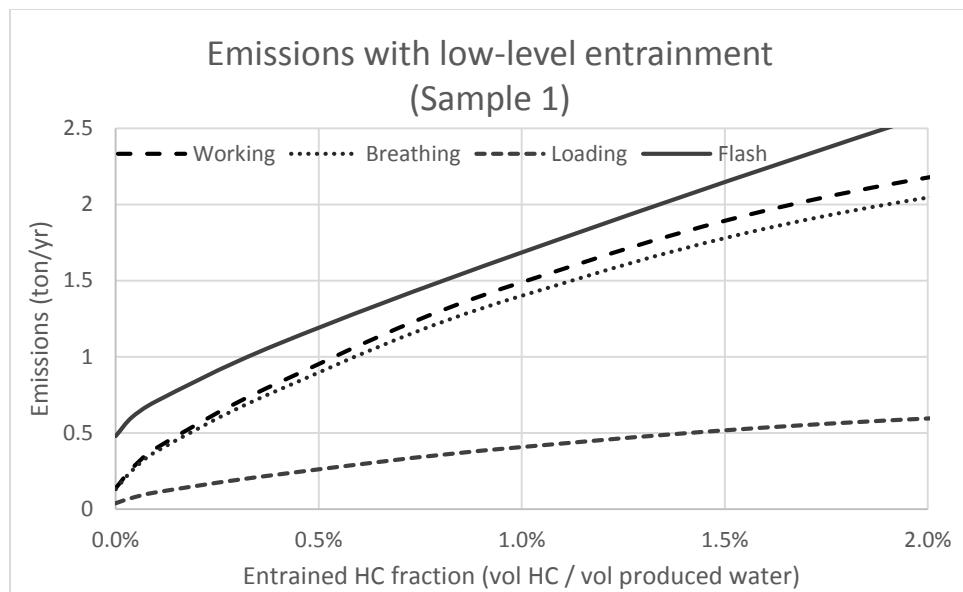
Figure 4e: Sample 1 emissions vs. entrained HC fraction (low entrained fractions)

Comparison of PPW method to common rules of thumb for estimating produced water emissions

This PPW method for calculating produced water storage tank emissions can now be compared to the various definitions of the "1% rule". A basic premise of the 1% rule is that at the upstream separator, the water and hydrocarbons were at thermodynamic equilibrium. It is assumed that the composition of the hydrocarbon stream leaving the separator is the same as the composition of any entrained hydrocarbons in the water, and that hydrocarbon composition may be used in estimating emissions from the produced water tank. In discussions with oil and gas industry professionals and in TCEQ documentation, four different definitions of the 1% rule were discovered. These are presented here, with the order from most common to least common in the author's informal survey. These all assume some method is available for calculating flashing losses, and that WB&L losses will be calculated with AP 42 methods for hydrocarbon storage tanks.

__Method A__—Use the produced water flowrate and the composition of the hydrocarbon streams when performing the calculations. Calculate flash, working, breathing and loading per AP 42, then multiply results by 1%.

This method will give reasonably accurate flash emissions from the entrained hydrocarbons since these emissions are proportional to the entrained hydrocarbon flowrate. However, this method will not account for the flash emissions from dissolved hydrocarbons in water. Further, this method will substantially underestimate WB&L losses as these losses do not decrease proportionally with incoming hydrocarbon flow.

Method B—*Use the produced water flowrate, multiplied by 1%, and the composition of the hydrocarbon stream when performing the calculations. Calculate flash, working, breathing and loading without further modification using AP 42.*

This method will yield the same flash estimates as Method A, and it will provide reasonable breathing losses. However, since the throughput of the tank is reduced to 1% of actual, changing tank levels are not appropriately considered, and the working/loading losses are underestimated.

Method C—*Use the produced water flowrate and a composition comprised of 99% water and 1% hydrocarbon stream when performing the calculations. Calculate flash emissions with a process simulator. Calculate working, breathing and loading without further modification using AP 42.*

This is the method published in a guideline from the Texas Commission on Environmental Quality (TCEQ) [4]. The guideline indicates that this method be used in conjunction with the software program *Tanks 4.09d* [5]*,* which uses Raoult's law to calculate vapor pressure. (*Tanks 4.09d* is a software program developed and distributed by the EPA, which implements the methods specified in AP 42 Chapter 7.)

The problem with this method is the use of Raoult's law in *Tanks 4.09d* to calculate the vapor pressure of the water/hydrocarbon mixture after the initial flash. Raoult's law will drastically under predict vapor pressure, resulting in significant under prediction of WB&L losses.

The flash predictions of this method will also be underestimated. When mixing 1 part hydrocarbon with 99 parts water, there is enough absorption of light hydrocarbon to significantly affect the vapor pressure of the remaining liquid hydrocarbons, thereby affecting emissions. In reality, the water is already saturated with the hydrocarbon components, and little to no additional absorption should take place.

Method D—*Use the produced water flowrate and a composition comprised of 99% water and 1% hydrocarbons when performing <u>flash</u> calculations. Use the produced water flowrate and the hydrocarbon composition when performing <u>WB&L</u> calculations with AP 42.*

This is another TCEQ guideline [6]. For flashing emissions, the results are identical to Method C, and are therefore underestimated due to absorption of hydrocarbons into the water. The WB&L emissions are very similar to that of the PPW method. This is logical since the vapor pressure used in the PPW method is essentially hydrocarbon vapor pressure. The slightly higher WB&L losses for Method D are due to the fact that there is less hydrocarbon depletion from the Method D flash, which leaves more material available for WB&L losses.

Figure 5 shows the flashing, working, breathing and loading losses of these four methods compared against the predictions of the PPW method. 1% by volume of hydrocarbons was assumed to be entrained, and the composition of Sample 2 was used. For all methods, the emissions of any component were capped at the incoming feed rate for that component.
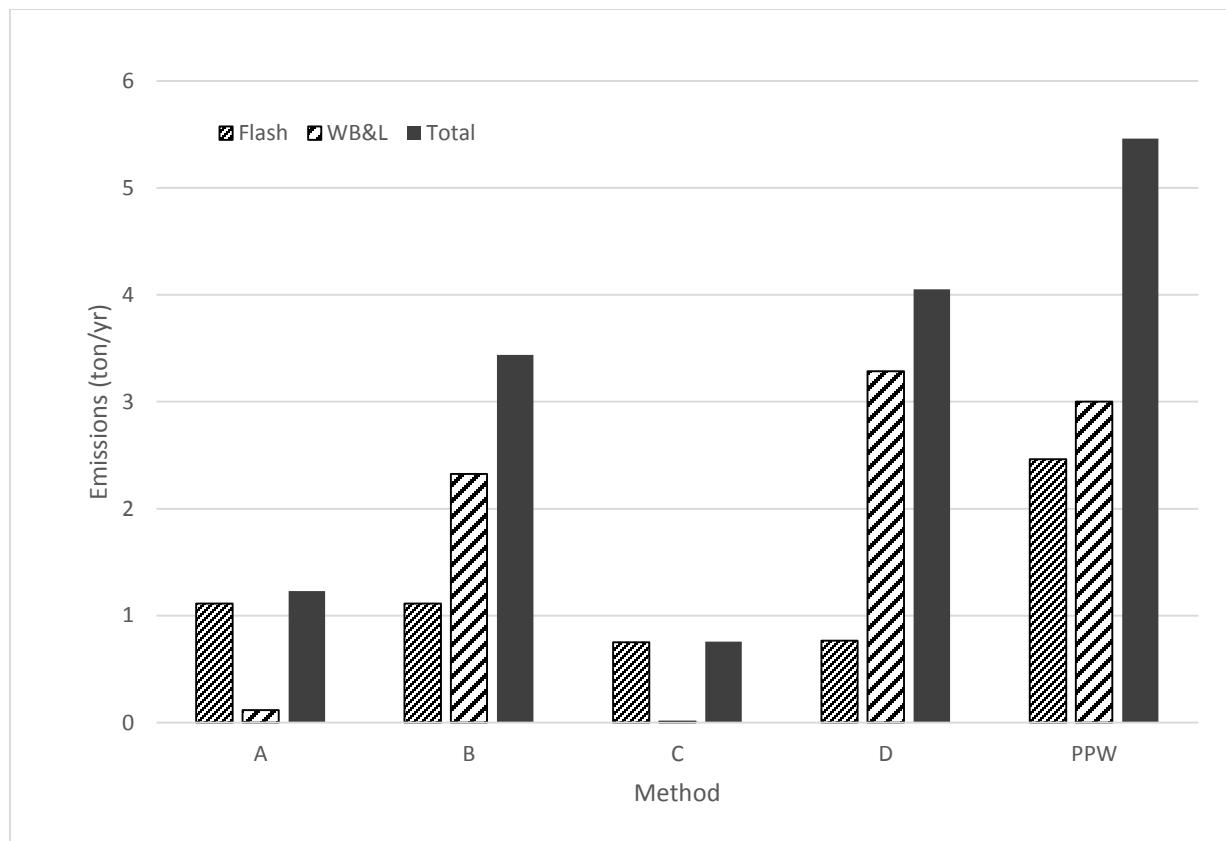
Figure 5: Emissions estimates using the various methods for hydrocarbon Sample 2, assuming 1% entrainment.

Conclusion

The AP 42 methodology is widely accepted for estimating hydrocarbon storage tank emissions and has been shown to give reasonable results for hydrocarbon tanks. There is a desire to apply a similar methodology for estimating produced water storage tank emissions, but typically the produced water composition or levels of hydrocarbon entrainment is unknown. The four methods presented here that rely on the use of AP 42 and the pressurized hydrocarbon liquid composition show deficiencies in some way and can produce significantly different emissions estimates.

A process simulator-based methodology, which can be easily automated, is presented here for calculating produced water emissions. This methodology uses the C&T component of AP 42, which is known to provide reasonable results, and replaces faulty vapor pressure predictions with rigorous process simulator predictions. Further, it captures the fact that with low entrainment fractions there can be significant depletion of lighter hydrocarbon components. Neglecting this can cause substantial over prediction of emissions.

A next step would be to compare the predictions of this new method against tank emissions measurements. The AP 42 C&T methods appear to be qualitatively correct. The trends predicted by the methods do track in the correct direction, but whether they should be modified for use with produced water emissions remains an open question.

References

[1] ProMax, 3.2.15289, Process Simulation Software, Bryan Research & Engineering, Inc., 2015.

[2] *AP 42 Compilation of Air Pollutant Emission Factors*, Vol. 1, 5th edition.

[3] *EPA Review of Available Documents and Rationale in Support of Final Emission Factors and Negative Determinations for Flares, Tank, and Wastewater Treatment Systems*, Environmental Protection Agency, Research Triangle Park, NC, 2015

[4] *Determining Emissions from Produced Water Storage Tanks*, Texas Commission on Environmental Quality.

[5] TANKS Emissions Estimation Software, Version 4.09D, Environmental Protection Agency, October 2006.

[6] *Emissions Representations for Produced Water*, Texas Commission on Environmental Quality, May 2012.