A greenhouse gas source of surprising significance: anthropogenic CO₂ emissions from use of methanol in sewage treatment

John L. Willis, Ahmed Al-Omari, Robert Bastian, Bill Brower, Christine DeBarbadillo, Sudhir Murthy, Christopher Peot and Zhiguo Yuan

ABSTRACT

The impact of methanol (CH₃OH) as a source of anthropogenic carbon dioxide (CO₂) in denitrification at wastewater treatment plants (WWTPs) has never been quantified. CH₃OH is the most commonly purchased carbon source for sewage denitrification. Until recently, greenhouse gas (GHG) reporting protocols consistently ignored the liberation of anthropogenic CO₂ attributable to CH₃OH. This oversight can likely be attributed to a simplifying notion that CO₂ produced through activated-sludge-process respiration is biogenic because most raw-sewage carbon is un-sequestered prior to entering a WWTP. Instead, a biogenic categorization cannot apply to fossil-fuel-derived carbon sources like CH₃OH. This paper provides a summary of how CH₃OH use at DC Water’s Blue Plains Advanced Wastewater Treatment Plant (AWTP; Washington, DC, USA) amounts to 60 to 85% of the AWTP’s Scope-1 emissions. The United States Environmental Protection Agency and Water Environment Federation databases suggest that CH₃OH CO₂ likely represents one quarter of all Scope-1 GHG emissions attributable to sewage treatment in the USA. Finally, many alternatives to CH₃OH use exist and are discussed.

Key words | anthropogenic greenhouse gas, global-warming mitigation, methanol, methodology, nitrogen removal, sewage treatment

INTRODUCTION

Many surface waters experience eutrophication caused by excessive nitrogen and phosphorus loading, and in response, the US Environmental Protection Agency (EPA) has regulated select wastewater treatment plant (WWTP) discharges for nitrogen and/or phosphorus. Large and notable regulated water bodies include the Chesapeake Bay, Lake Erie, Lake Ontario, Lake Michigan, Lake Huron, Long Island Sound, and Puget Sound. The EPA’s Clean Water Needs Survey (CWNS 2008) indicates that 284 WWTPs in the USA denitrify their effluent and almost 200 of those use methanol (CH₃OH) as a carbon source to enable that process (Theis & Hicks 2012). The number of WWTPs, nitrogen removal levels required, and associated CH₃OH use are expected to increase in the USA and globally as time evolves.

Most greenhouse gas (GHG) reporting protocols currently do not account for the conversion of CH₃OH to CO₂ and its subsequent release as an anthropogenic emission, largely because all CO₂ evolving from WWTPs is assumed to be biogenic. Instead, CH₃OH is derived from natural gas, which is a fossil fuel, and is introduced by WWTP operations staff. In 2012, the organization formerly called the ‘International Council for Local Environmental Initiatives’ (now referred to simply as ‘ICLEI’) published their US Community Protocol (ICLEI 2012) with methodology WW.9 for ‘Process carbon dioxide emissions from the use of fossil-fuel-derived methanol for biological nitrogen removal’ to more appropriately account for this phenomenon.

Scope of study

This paper presents the significance of CH₃OH-derived CO₂ to the GHG emissions inventory of DC Water’s (Washington, DC, USA) Blue Plains Advanced Wastewater
Treatment Plant (AWTP). Blue Plains is a very large facility, treating an average of over 13 m³/s of domestic sewage from a population of over 2.2 million people in the District of Columbia and surrounding counties in Maryland and Virginia. Sewage is treated to very stringent effluent phosphorus standards and what is referred to as ‘limit of technology’ effluent-nitrogen standards. The impact of including a site-specific application of ICLEI’s WW.9 methodology to account for anthropogenic CO₂ from CH₃OH is used to demonstrate that this previously overlooked emission can be extremely significant for a WWTP with nitrogen removal requirements.

The Blue Plains AWTP’s GHG emissions were analyzed before and after recent sludge processing upgrades to enhance the quality and reduce the quantity of biosolids while enabling production of renewable power. The plant’s Scope-1 emissions and national databases were then used to estimate that approximately one quarter of all wastewater-treatment direct GHG emissions are attributable to CH₃OH – a staggering high amount for a previously overlooked emissions source. Finally, options are presented for reducing and/or eliminating CH₃OH GHG emissions while meeting effluent nitrogen requirements.

**Wastewater nitrogen removal processes**

WWTPs have conventionally removed ammonia (NH₃) in influent sewage through nitrification and denitrification (EPA 2007). Through the nitrification process, NH₃ is converted to nitrate (NO₃⁻) in the presence of oxygen (O₂). The stoichiometry for this two-stage process is as follows:

1. NH₃ oxidized to nitrite (NO₂⁻): NH₃ + O₂ → NO₂⁻ + 3H⁺ + 2e⁻
2. NO₂ oxidized to (NO₃⁻): NO₂⁻ + H₂O → NO₃⁻ + 2H⁺ + 2e⁻

In the subsequent stage under anoxic conditions, NO₃ is biologically reduced to N₂ gas and released to the atmosphere. The biology will only use NO₃ oxygen when limited dissolved O₂ is available, as dissolved O₂ is a preferred oxygen source. Additionally, for the denitrification process to take place, a readily degradable carbon/food source like CH₃OH is needed. The denitrification stoichiometry with a CH₃OH substrate is as follows:

3. Denitrification: 6NO₃⁻ + 5CH₃OH → 5CO₂ + 3N₂ + 7H₂O + 6OH⁻

**GHG accounting protocols**

Most GHG accounting protocols (WRI & WBCSD 2004; IPCC 2006b; CARB 2008; TCR 2008; Australian National Greenhouse Accounts 2013; Australian Government Department of the Environment 2013) – at least by omission if not overtly – assume that all CO₂ emitted from processing/conversion of wastewater carbonaceous oxygen demand (COD) is biogenic. ICLEI’s WW.9 methodology identified that CH₃OH used as a carbon source at WWTPs for biological nutrient removal (BNR) would generate Scope-1 anthropogenic CO₂ emissions. Scope-1 GHG emissions are actual GHGs evolving from combustion of fossil fuels or direct release of more potent GHGs. Scope-2 emissions, which tend to dominate WWTP reportable inventories, are emissions that are Scope-1 emissions for an outside party that produces energy (typically electricity but could also be purchased heat) used at the reporting facility. While Scope-2 emissions do not actually occur on site, the amount consumed at a WWTP is controlled by the utility. Most accounting protocols require that totals of Scopes 1 and 2 are reported.

IPCC (2006b) accounts for CH₃OH manufacturing emissions factors using a number of manufacturing-process-specific methodologies. Direct GHG emissions from the production process, classified as Scope-1, are the responsibility of the manufacturer. Similarly, power and heat purchased for CH₃OH manufacture are accounted for as Scope-2 emissions at the production facility. The combination of Scope-1 and Scope-2 manufacturing emissions results in a default emissions factor of 0.67 tonne CO₂e/tonne CH₃OH (assuming conventional steam reforming, without primary reformer as the default process).

For the WWTP, however, these manufacturing emissions are classified as a Scope-3 emission (not directly attributable to the WWTP itself) and are often excluded from GHG emissions inventories. Scope-3 emissions are those emissions that are either Scope-1 or Scope-2 for an outside or third-party entity, but the amount that the third party emits are directly affected by the actions of the reporting entity. In the case of the methanol manufacturer, proportionately more GHG emissions would be produced if the WWTP used more methanol. The WWTP could include the methanol manufacturer’s emissions as Scope-3 emissions. These third-party manufacturing emissions are discussed but not included in the Scope-1 and -2 GHG emissions totals herein.

ICLEI’s method WW.9 uses an 80% conversion factor of CH₃OH carbon to emitted CO₂ from a WWTP’s biological treatment process; the balance of the carbon is assumed to be converted to cell mass. The method differentiates the
following disposition for the CH$_3$OH-derived cell mass carbon as a function of the WWTP’s specific solids-disposition category.

- If raw solids are dried or directly disposed of without further processing, the remaining produced cell mass is assumed to remain intact without further destruction of cell mass carbon and liberation of CO$_2$. These practices would result in a net release of 80% of the fed CH$_3$OH carbon as CO$_2$.
- If produced solids are digested or stabilized using a biological process, it is assumed that half of the cell-bound carbon would be liberated and converted to CO$_2$, resulting in a 90% overall release of CH$_3$OH carbon as CO$_2$.
- In anaerobic digestion, cells would first be released as a combination of methane (CH$_4$) and CO$_2$, before the CH$_4$ is assumed to be burned and fully converted to CO$_2$.
- If raw sludge is incinerated or thermally destroyed, all cell carbon is assumed to be released as CO$_2$. Accordingly, 100% of CH$_3$OH fed to the WWTP would be converted to CO$_2$.

If the fate of CH$_3$OH-derived, activated-sludge carbon is better known through an alternative method, actual treatment plant data could be used instead of the defaults provided. DC Water has developed a site-specific methodology based on the ICLEI methodology but using Blue-Plains-AWTP-specific data for cell yield. However, they have not had enough run time with the new digesters or performed specific bench-scale tests to determine the fate of the CH$_3$OH-derived cell mass in the anaerobic-digestion process. As a result, the ICLEI 50%-further-destruction assumption is still used.

### Blue Plains AWTP performance

DC Water’s Blue Plains AWTP, as a WWTP meeting enhanced nitrogen removal (ENR) standards, demonstrates the relative significance of CH$_3$OH-induced, anthropogenic CO$_2$ evolution within a GHG emissions context. The difference between emissions with (now/post-digestion upgrades) and without (pre-digestion upgrades) enhanced anaerobic digestion and associated high-nitrogen-content recycle loads will be highlighted.

The AWTP’s treatment flow path consists of preliminary treatment; primary sedimentation; high-rate, carbonaceous, coarse-bubble, air-activated sludge; B-stage, nitritification/denitritification fine-bubble, air-activated sludge; chlorine disinfection; filtration; and de-chlorination. Figure 1 shows the Blue Plains flow train and solids processing in operation until the end of 2014; solids processing included separate gravity thickening for primary sludge and dissolved-air flotation thickening for secondary and nitritification waste activated sludge, centrifuge dewatering, and lime stabilization.

Figure 2 schematically depicts plant processes currently in place after construction of new solids handling upgrades which include sludge-screening, centrifuge pre-dewatering, thermal hydrolysis, anaerobic digestion, and belt-filter press final dewatering processes that went into service at the beginning of 2015. However, combustion-turbine-based combined heat and power (CHP) was not consistently operating until after June 2015, requiring the boilers to use digester gas and/or natural gas to produce steam to heat the digestion pretreatment system. The boilers were fed...
exclusively natural gas initially but the fuel was switched to digester gas once the stable anaerobic-digestion process produced enough digester gas. During normal operation, digester gas will fuel the electricity- and steam-producing turbines (and boilers, but only in a back-up mode).

**Nitrogen performance and CH₂OH use**

The AWTP’s performance from 1 January 2012 to 30 July 2015 is used for this case study. Figure 3 shows the nitrification process influent (inclusive of recycles) and effluent total nitrogen mass, and volume of CH₂OH used within the process, including daily performance and 30-day rolling averages. Prior to starting up the plant upgrades in the beginning of 2015, Blue Plains produced effluent with total-nitrogen concentrations averaging just below 4.0 mg/L while using 49,000 to 57,000 L/D of CH₂OH. The CH₂OH purchased by DC Water is virtually pure and is assumed to be 100% CH₂OH in their GHG calculations and in this paper; during this period, the AWTP’s solids were lime-stabilized and beneficially reused without a significant sidestream-NH₃ or ammonium (NH₄⁺) source.

DC Water brought its new Cambi® thermal-hydrolysis anaerobic-digestion process on line over a 4-month period at the end of 2014 before becoming fully operational at the beginning of 2015. Cambi uses thermal hydrolysis to ‘pressure cook’ dewatered sludge solids at 150 psig and 165 degrees C upstream of digestion, increasing the amount of solids converted to biogas, and sterilizing and improving dewaterability/final solids content of the biosolids product. The solids upgrades increased daily measured CH₂OH consumption by approximately 54 percent to between 76,000 and 87,000 L/D, in order to treat NH₃/NH₄⁺ produced in the digesters that is recycled to the nitrification/denitrification activated-sludge process. Plant-effluent total nitrogen was also reduced to an average of 3.3 mg/L during the first 6 months of 2015.

**Site-specific methylotroph observed yield for Blue Plains AWTP**

A site-specific yield rate for methylotrophs was developed for DC Water that considers measured and operation-specific kinetics in lieu of the ICLEI rule’s default of 0.20 g COD/g COD. The calculation uses an ideal CH₂OH cell yield of 0.40 mg COD/mg COD based on Dold’s research (Dold et al. 2008) conducted at Blue Plains; this yield is lower than for other influent COD sources, indicating that a higher percentage of the CH₂OH carbon is released as CO₂ directly from the biological process. The following equation is used to derive methylotroph observed
yields from the Blue Plains nitrification and denitrification activated-sludge processes:

\[
Y_{\text{obs}} = \text{methyltrophs} + \text{cell debris}
\]

\[
Y_{\text{obs}} = \frac{Y + f_d \cdot Y + b \cdot \text{SRT}}{(1 + b \cdot \text{SRT})}
\]

\[
= \frac{1 + b \cdot \text{SRT}}{1 + b \cdot \text{SRT}} \cdot \left(1 + b \cdot \text{SRT}\right)
\]

where:

- \( Y_{\text{obs}} \) = observed yield
- \( Y \) = theoretical yield
- \( f_d \cdot Y + b \cdot \text{SRT} \)
- \( (1 + b \cdot \text{SRT}) \)
- \( b_{ae} \) = aerobic methylotroph decay rate
- \( b_{ax} \) = anoxic methylotroph decay rate
- \( \text{SRT}_{ae} \) = aerobic solids retention time
- \( \text{SRT}_{ax} \) = anoxic solids retention time
- \( f_d \) = fraction of biomass remaining as cell debris

With digestion recently brought on line, the ICLEI assumption that half of the remaining \( \text{CH}_3\text{OH} \)-derived cell mass would be liberated as \( \text{CO}_2 \) is used. The assumed yields pre- and post-digestion are 0.132 and 0.066 gCOD\text{bio}/gCOD\text{CH}_3\text{OH}, respectively.

As a further clarification, biogas (approximately 60% \( \text{CH}_4 \) and 40% \( \text{CO}_2 \)) is produced when cell mass is destroyed. At Blue Plains biogas is either beneficially used as a fuel in CHP or boilers, or burned using a high-efficiency waste-gas flare. Under any scenario, \( \text{CH}_4 \) is completely oxidized and released as \( \text{CO}_2 \). Accordingly, additional cell carbon released in digestion is assumed to ultimately be emitted in \( \text{CO}_2 \) form.

The COD-based values must be adjusted to account for the carbon mass per unit COD in \( \text{CH}_3\text{OH} \) and the biomass, respectively. The conversion for \( \text{CH}_3\text{OH} \) is fairly straightforward, as follows:

- Carbon fraction of \( \text{CH}_3\text{OH} \)
  
  \[
  = \frac{m_C}{m_{\text{CH}_3\text{OH}}} = \frac{12}{(12 + 5 + 16 + 1)} = 0.375 \text{ gC}_{\text{CH}_3\text{OH}}/\text{gCH}_3\text{OH}
  \]
  
  \[
  \text{COD per gram } \text{CH}_3\text{OH} = 1.50 \text{ gCOD}_{\text{CH}_3\text{OH}}/\text{gCH}_3\text{OH}
  \]
  
  \[
  \text{grams C per gram } \text{CH}_3\text{OHCOD} = 0.375 \text{ gC/gCH}_3\text{OH}/1.50 \text{ gCOD}_{\text{CH}_3\text{OH}}/\text{gCH}_3\text{OH} = 0.25 \text{ gC/gCOD}_{\text{CH}_3\text{OH}}
  \]
The conversion for biomass depends upon the assumed carbon content and COD per unit volatile suspended solids in the biomass (VSS\textsubscript{Bio}):

Carbon fraction of biomass (Ekama 2009)
\[ = 0.52 \text{ gC/gVSS\textsubscript{Bio}} \]

COD per gram of biomass = 1.48 gCOD\textsubscript{Bio}/gVSS\textsubscript{Bio}
\[ = 0.52 \text{ gC\textsubscript{Bio}/gVSS\textsubscript{Bio}} / 1.48 \text{ gCOD\textsubscript{Bio}/gVSS\textsubscript{Bio}} = 0.35 \text{ gC\textsubscript{Bio}/gCOD\textsubscript{Bio}} \]

Using these per-unit-COD-corrected carbon concentrations changes the original yield equation as follows for the carbon balance:

\[ Y_{\text{obs-C-PreUp}} = 0.132 \text{ gCOD\textsubscript{bio}/gCOD\textsubscript{CH}_3\text{OH}} \]
\[ \times 0.35 \text{ gC\textsubscript{bio}/gCOD\textsubscript{bio}} / 0.25 \text{ gCH}_3\text{OH/gCOD\textsubscript{CH}_3\text{OH}} = 0.185 \text{ gC\textsubscript{bio}/gCH}_3\text{OH} \]
\[ Y_{\text{obs-C-PostUp}} = Y_{\text{obs-C-PreUp}} \times 50\% \]
\[ = 0.185 \text{ gC\textsubscript{bio}/gCH}_3\text{OH} \times 50\% = 0.0925 \text{ gC\textsubscript{bio}/gCH}_3\text{OH} \]

The converse of the carbon cell yield equals the amount of carbon liberated to the atmosphere. The Blue Plains AWTP anthropogenic CO\textsubscript{2} emission rates for the pre- and post-digestion upgrades for CH\textsubscript{3}OH addition are therefore:

\[ \text{ER}_{\text{CO}_2-\text{PreUp}} = \frac{(1 - Y_{\text{obs-C-PreUp}}) \times \rho_{\text{CH}_3\text{OH}} \times m_{\text{C}} / m_{\text{CH}_3\text{OH}} \times m_{\text{CO}_2} / m_{\text{C}}}{12 + 16 + 2} / 12 = 0.886 \text{ kgCO}_2/\text{L-CH}_3\text{OH} \]
\[ \text{ER}_{\text{CO}_2-\text{PostUp}} = (1 - Y_{\text{obs-C-PostUp}}) \times \rho_{\text{CH}_3\text{OH}} \times m_{\text{C}} / m_{\text{CH}_3\text{OH}} \times m_{\text{CO}_2} / m_{\text{C}} \]
\[ = (1 - 0.0925) \times 0.791 \times 0.375 \times (12 + 16 + 2) / 12 = 0.987 \text{ kgCO}_2/\text{L-CH}_3\text{OH} \]

where:
\[ \text{ER} = \text{emission rate in kg CO}_2/\text{L-CH}_3\text{OH fed to process} \]
\[ \rho_{\text{CH}_3\text{OH}} = \text{density of CH}_3\text{OH} = 0.791 \text{ kg/L} \]

GHG emissions over the period of study

DC Water has maintained a GHG emissions inventory since 2007 in anticipation of a number of energy-consumption-reducing, renewable-power-generating, and GHG-lowering improvements that are almost all on line now (the exception being a sidestream deammonification process that will be commissioned in 2017). Table 1 summarizes the total Scope-1 and -2 emissions for the Blue Plains AWTP over calendar years 2012, 2013, 2014, and the first half of 2015.

<table>
<thead>
<tr>
<th>Emission Source</th>
<th>2012 Annual Emissions Estimate, Metric Tons CO\textsubscript{2}e</th>
<th>2013 Annual Emissions Estimate, Metric Tons CO\textsubscript{2}e</th>
<th>2014 Annual Emissions Estimate, Metric Tons CO\textsubscript{2}e</th>
<th>2012 through 2014 Average Annual Emissions Estimate, Metric Tons CO\textsubscript{2}e</th>
<th>First Half (6 months) of 2015 Emissions Estimate, Metric Tons CO\textsubscript{2}e</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Scope 1</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Natural Gas</td>
<td>2,237</td>
<td>3,745</td>
<td>2,369</td>
<td>2,784</td>
<td>4,558</td>
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<tr>
<td>Vehicle Fuel</td>
<td>3,004</td>
<td>2,029</td>
<td>1,581</td>
<td>2,205</td>
<td>518</td>
</tr>
<tr>
<td>Refrigerants</td>
<td>217</td>
<td>0</td>
<td>0</td>
<td>72</td>
<td>0</td>
</tr>
<tr>
<td>CO\textsubscript{2} from Addition of Methanol</td>
<td>1,6376</td>
<td>16,976</td>
<td>16,953</td>
<td>16,768</td>
<td>14,702</td>
</tr>
<tr>
<td>Process N\textsubscript{2}O</td>
<td>931</td>
<td>874</td>
<td>798</td>
<td>868</td>
<td>460</td>
</tr>
<tr>
<td>Effluent Discharge N\textsubscript{2}O</td>
<td>2,302</td>
<td>2,221</td>
<td>2,690</td>
<td>2,404</td>
<td>1,109</td>
</tr>
<tr>
<td><strong>Total Scope 1</strong></td>
<td>25,068</td>
<td>25,846</td>
<td>24,389</td>
<td>25,101</td>
<td>21,147</td>
</tr>
<tr>
<td><strong>Scope 2</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electricity</td>
<td>105,864</td>
<td>109,795</td>
<td>117,174</td>
<td>110,944</td>
<td>54,127</td>
</tr>
<tr>
<td><strong>Total with Scopes 1 and 2</strong></td>
<td>130,932</td>
<td>135,641</td>
<td>141,563</td>
<td>136,045</td>
<td>75,274</td>
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</table>
Pre-digestion performance over 2012 through 2014 is averaged for comparison with the first half of 2015, when anaerobic digestion was operational. Table 2 presents these same data normalized to metric tons (MT) of CO\textsubscript{2}e emissions per month for before and after the upgrades. The Table 2 post-upgrade emissions have been modified to better simulate operation when the combustion turbines consistently use digester biogas as a renewable fuel for CHP. The adjustments made to the data presented in Table 1 and shown in Table 2 are as follows.

- Natural gas consumption was considerably higher during Cambi and digestion start-up, as that fossil fuel was used by boilers to produce steam before the digesters were producing enough digester gas; this is a condition that only occurs during process start-up and is not expected to be required at any future time. Accordingly, the natural gas emissions in Table 2 have been set at the average for 2012 to 2014 of 232 MT CO\textsubscript{2}e/month instead of the actual rate of 726 MT CO\textsubscript{2}e/month.

- The digester-gas-fired combustion turbines were started later than the rest of the Cambi-digestion process and were only running consistently after the analyzed period. During the first six months of 2015, the AWTP used an average of 25 to 26 megawatts (MW) of purchased electricity. The turbines are projected to produce an average net output of slightly over 10 MW. Based on this, the AWTP’s grid power consumption for the first half of 2015 has been reduced by exactly 40 percent, reducing associated GHG emissions from 9,021 to 5,413 CO\textsubscript{2}e/month during that same period.

Figure 4 uses the adjusted data (from Table 2) to show the relative contribution of each emission source to the AWTP’s emissions totals for Scope-1 and -2 combined, and for Scope-1 alone, for the pre- and post-digestion operational periods. While it is important to recognize that the sample set for post-digestion is much smaller and includes perturbations associated with various process start-ups, some observations include the following.

(1) From a Scope-1 perspective, CO\textsubscript{2} emissions attributable to CH\textsubscript{3}OH are extremely significant, representing 66.8%

### Table 2

<table>
<thead>
<tr>
<th>Emission Source</th>
<th>2012 Average Monthly Emissions Estimate, Metric Tons CO\textsubscript{2}e</th>
<th>2013 Average Monthly Emissions Estimate, Metric Tons CO\textsubscript{2}e</th>
<th>2014 Average Monthly Emissions Estimate, Metric Tons CO\textsubscript{2}e</th>
<th>2012 through 2014 Average Annual Emissions Estimate, Metric Tons CO\textsubscript{2}e</th>
<th>Adjusted\textsuperscript{a, b} First Half of 2015 Average Monthly Emissions Estimate, Metric Tons CO\textsubscript{2}e</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Scope 1</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Natural Gas\textsuperscript{a}</td>
<td>186</td>
<td>312</td>
<td>197</td>
<td>232</td>
<td>232</td>
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<tr>
<td>Vehicle Fuel</td>
<td>250</td>
<td>169</td>
<td>132</td>
<td>184</td>
<td>86</td>
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<td>18</td>
<td>0</td>
<td>0</td>
<td>6</td>
<td>0</td>
</tr>
<tr>
<td>CO\textsubscript{2} from Addition of CH\textsubscript{3}OH</td>
<td>1,365</td>
<td>1,415</td>
<td>1,413</td>
<td>1,397</td>
<td>2,450</td>
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<td>Process N\textsubscript{2}O</td>
<td>78</td>
<td>73</td>
<td>66</td>
<td>72</td>
<td>77</td>
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<tr>
<td>Effluent Discharge N\textsubscript{2}O</td>
<td>192</td>
<td>185</td>
<td>224</td>
<td>200</td>
<td>185</td>
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<tr>
<td><strong>Total Scope 1</strong></td>
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<td>2,154</td>
<td>2,032</td>
<td>2,092</td>
<td>3,030</td>
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<td><strong>Scope 2</strong></td>
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<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Electricity\textsuperscript{b}</td>
<td>8,822</td>
<td>9,150</td>
<td>9,764</td>
<td>9,245</td>
<td>5,413</td>
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<tr>
<td><strong>Total with Scopes 1 and 2</strong></td>
<td>10,911</td>
<td>11,303</td>
<td>11,797</td>
<td>11,337</td>
<td>8,443</td>
</tr>
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</table>

\textsuperscript{a}First half of 2015 monthly natural gas emissions are reduced from actual rates of 726 MT CO\textsubscript{2}e/month to the prior-3-year-average rate of 232 MT CO\textsubscript{2}e/month eliminating consumption for digester start-up.

\textsuperscript{b}First half of 2015 monthly electricity emissions are reduced from actual of 9021 CO\textsubscript{2}e/month to a projected 5,413 CO\textsubscript{2}e/month assuming biogas-fueled CHP was online, offsetting 40% of the AWTP’s power consumption.
and 80.8% of Blue Plains’ Scope-1 emissions for pre- and post-digestion, respectively. CH₃OH CO₂ is 6 to 10.5 times as significant as the next most significant Scope-1 emissions source: natural gas use. Post-digestion CH₃OH CO₂ increased by 1,050 MT CO₂e/month (or 75%) due to increases in CH₃OH use compounded by the increased CO₂-emission rate with digestion of activated-sludge cell mass.

(2) From a combined Scope-1-and-2 perspective, CH₃OH-related emissions are still significant, although not as significant as electricity consumption. CH₃OH CO₂ represents 12.3% and 29.0% of Blue Plains’ Scope-1 and-2 emissions for pre- and post-digestion, respectively. The high post-digestion operation value (29%) is due to increased CH₃OH CO₂ and the reduction in Scope-2 electricity emissions (representing a 34% reduction compared to the entire pre-digestion inventory).

(3) Digester-gas-fueled-CHP Scope-2 reductions are being made subsequent to fine-bubble-diffuser retrofits that reduced the AWTP’s average electrical consumption from approximately 32 MW to 25.5 MW. Together the two projects represent a 50% reduction in grid-purchased power.

(4) If Scope-3 manufacturing emissions were added to the presented inventories, the pre- and post-digestion CH₃OH-related emissions would be increased by 891 and 1,404 MT CO₂e/month, respectively, increasing the apparent CH₃OH impact by 64% and 57%.

(5) It might occur to some that by adding advanced digestion to Blue Plains, Scope-1 emissions increase by 12,600 MT CO₂e/yr and Scope-3 manufacturing emissions would have added another 6,150 CO₂e/yr. This would beg the question: were the upgrades worthwhile from a GHG perspective? Fortunately, the following factors more than entirely offset CH₃OH-use-associated increases:
(a) 46,000 MT CO₂e/yr reduced Scope-2 emissions from purchased electricity.
(b) 5,700 MT CO₂e/yr Scope-3 improvement in reduced biosolids-hauling fuel-consumption.
(c) 12,600 MT CO₂e/yr Scope-3 emissions reduction associated with lime manufacture.

These reductions and CH₃OH-related increases result in a net reduction of 45,000 MT CO₂e/yr while simultaneously reducing effluent total nitrogen by 17%.

In addition to reducing GHG emissions, the upgrades are also projected to save between $25 and $35 million per year for DC Water and the utility’s rate payers through parallel reductions in biosolids hauling/beneficial use costs, lime purchases, and power purchases.

**US national significance of wastewater CH₃OH use**

A few basic assumptions are needed to assess the significance of CO₂ emissions from wastewater CH₃OH use on a national scale. As CH₃OH use is largely dictated by effluent nitrogen requirements, the amount of wastewater treated to comply with graduated total-nitrogen-treatment standards must be known. Additionally, WWTPs meeting ENR standards are more likely to be heavily dependent on CH₃OH use than those meeting less stringent BNR standards.

Finally, use of anaerobic digestion creates a significant internal source of NH₃/NH₄⁺ that further increases CH₃OH demand.

Table 3 summarizes data from EPA’s (2016) Discharge Monitoring Report (DMR) Pollutant Loading Tool for calendar years 2007, 2010, 2012, 2014, and 2015. Figure 5 depicts flow treated by identified WWTP categories over those same reporting years. The downloaded DMR data have been summarized and adjusted as follows.

- Approximately one or two manual modifications were made each year to correct for anomalous data for plants identified as treating over 8 m³/s (or 180 million gallons per day, based on units in the DMR database) but known to be treating much less (e.g., almost-certainly inaccurate data whose overestimations of flow would have incorrectly skewed the results; these plants would appear with large flows in one year and not in any of the other years downloaded from the DMR database).
- The following ranges of effluent total nitrogen concentrations were used to classify facilities:
  1. Greater than 10.0 mg/L as ‘Secondary’ or ‘Sec’.
  2. Between 4.0 and 10.0 mg/L as ‘BNR’.
  3. Between 2.5 and 4.0 mg/L as ‘ENR’.
  4. Reporting effluent nitrogen less than 2.5 mg/L as ‘Undetermined’ based on two factors:
    - an attempt to define a threshold where a reasonable match could be made for the 284 ENR plants and 200 plants using CH₃OH in 2006 that were mentioned previously (CWNS 2008; Theis & Hicks 2012); and
    - the fact that there are few, if any, WWTPs averaging less than 2.5 mg/L total nitrogen; suggesting that the plants in the database with these values likely fall into one of the other three classifications.

The number of WWTPs using anaerobic digestion is also needed for context due to the process significance on plant NH₃ load, resulting CH₃OH demand, and total Scope-1 GHG emissions (as evidenced by the Blue Plains AWTP where CH₃OH use increased by 54% and overall GHG emissions increased by 75%). Table 4 presents data developed from the Biogas Production and Use at Water Resource Recovery Facilities in the United States database of the Water Environment Federation (WEF) (Qi & Beecher 2015). These data were used in lieu of EPA’s DMR data due to EPA’s acknowledged short comings within their own database concerning the infrastructure in place at specific WWTPs (many of which have not been updated since the mid-1980s). The WEF effort was specifically initiated in 2012 to update EPA data and used a combination of the 2008 and 2012 DMR data as a foundation. The WEF data have not been modified and have been grouped into the following three digestion classifications.

1. ‘Digesters with advanced gas use’ includes WWTPs with anaerobic digestion that use biogas in engine-driven process equipment, internal combustion engines, turbines, or microturbines, or inject into a natural gas pipeline.
2. ‘Digesters with no or unknown advanced gas use’ includes plants that only use biogas to produce heat for the digesters or building heating. Plants known to have digesters but whose gas use was listed as ‘unknown’ are also included in this class.
3. ‘No or unknown digesters’ includes WWTPs that do not have or were not confirmed to have anaerobic digestion.

The final factor used to assess CH₃OH use on a national scale is proportional allocation of Blue Plains GHG emissions to plants operating in various combinations of effluent performance and presence of anaerobic digestion and biogas use. Table 5 shows how the DC Water Scope-1...
Table 3 | Summary of all NPDES discharges for select calendar years from 2007 to 2015 by effluent total nitrogen category. Number of facilities, total daily flows, percent of determined flow (calculated by adding secondary, BNR, and ENR flows and excluding undetermined flows), and percent of total flow (including undetermined flows) are presented. The 2007 data, while provided for context, do not align with other reported years; having considerably lower flows/numbers of facilities and divergent trends in permit conditions that are suggestive of a change in sample approach or at very least response completeness. As such, 2007 data have been excluded from the subsequent analyses.

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<td></td>
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<td>209</td>
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<td>44</td>
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<td>4,421</td>
<td>455</td>
<td>4,878</td>
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<td>957</td>
<td>8,151</td>
<td>1,064</td>
<td>8,284</td>
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% of Sec + BNR + ENR Flow | % Total Flow | % of Sec + BNR + ENR Flows | % Total Flow | % of Sec + BNR + ENR Flows | % Total Flow | % of Sec + BNR + ENR Flows | % Total Flow | % of Sec + BNR + ENR Flows | % Total Flow | % of Sec + BNR + ENR Flows | % Total Flow |
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<td>Sec</td>
<td>Over 10.0</td>
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<td>21.8%</td>
<td>48.6%</td>
<td>27.2%</td>
<td>50.0%</td>
<td>29.8%</td>
<td>45.4%</td>
<td>25.0%</td>
<td>39.0%</td>
<td>22.7%</td>
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<tr>
<td>BNR</td>
<td>Under 10.0</td>
<td>47.3%</td>
<td>24.8%</td>
<td>44.0%</td>
<td>24.6%</td>
<td>41.9%</td>
<td>25.0%</td>
<td>45.0%</td>
<td>24.8%</td>
<td>49.0%</td>
<td>28.6%</td>
</tr>
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<td>ENR</td>
<td>Under 4.0</td>
<td>11.1%</td>
<td>5.8%</td>
<td>7.5%</td>
<td>4.2%</td>
<td>8.1%</td>
<td>4.8%</td>
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<td>5.3%</td>
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<td>NA</td>
<td>40.4%</td>
<td>NA</td>
<td>44.8%</td>
<td>NA</td>
<td>41.7%</td>
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NA: not applicable.
emissions have been adjusted to cover the range of plants. These adjustments are entirely based on the authors’ educated judgment, as no reference currently exists covering such permutations. These approximations are considered ‘likely’ and based on the following aspects of the Blue Plains AWTP’s unique operations relative to the rest of the nation’s WWTPs.

- Because of its two-stage activated-sludge configuration with a carbonaceous ‘A-stage’ followed by ‘B-stage’ that nitrifies and denitrifies, Blue Plains has very limited indigenous carbon in the influent to its B-stage. The upstream high-rate treatment process removes this potential substrate that could be used to denitrify NO₂ or NO₃ at most other plants with BNR or ENR limits. Most other plants would use this raw-sewage carbon to offset a portion of the Blue Plains CH₃OH dose. Because of this, other ENR plants would likely use only 75% and 50% of Blue Plains’ supplemental carbon use with and without digestion, respectively. Multiplying each of these carbon-demand factors by 70.4% (200 of 284 ENR WWTPs use CH₃OH (CWNS 2008)) proportionately accounts for the fact that not all supplemental-carbon-dosing WWTPs use CH₃OH. Table 5 shows the combined methanol extrapolation factors based on both adjustments: 35.2% for ENR plants without digestion and 52.8% with digestion.

- For plants with less stringent BNR-effluent-nitrogen requirements, less nitrogen is removed and less surplus carbon would be needed. The authors are not aware of any BNR plants without anaerobic digestion using CH₃OH and, therefore, no CH₃OH use is assumed for that classification. Many large BNR WWTPs with digestion are known to use supplemental carbon (26th Ward, Wards Island, and Hunts Point plants operated by the New York City Department of Environmental Protection (NYCDEP), as examples). BNR plants with digestion are assumed to use 20% of Blue Plains’ carbon use, modified to account for the 70.4% of WWTPs using CH₃OH, for a combined factor of only 14.1% that of Blue Plains.

- Secondary WWTPs are not required to remove nitrogen and no CH₃OH use is assumed.

The above bases are used to create the estimates of national GHG emissions (Table 6) that suggest that over 25% of all Scope-1 emissions from wastewater treatment in the USA are attributable to CH₃OH use. While a number of assumptions have gone into and have been potentially compounded in this determination, CH₃OH use at a BNR or ENR WWTP almost certainly represents a very significant component of that facility’s GHG emissions. As such, it becomes critical that this previously unaccounted-for GHG contribution be included in future GHG accounting.
Options for reducing the anthropogenic CO₂ emissions attributable to CH₃OH

Because of its significance, opportunities to reduce and/or eliminate CH₃OH use should be considered. Some more common methods that are fairly widely used today include the following.

1. **Use of other renewable carbon substrates.** Options include the following:

   a. Glycerol, which is in use at NYCDEP plants including Hunts Point, 26th Ward, and Wards Island, and pilot tested by the Washington Suburban Sanitary Commission (Prince George’s and Montgomery Counties, MD, USA) at their Parkway plant (Selock et al. 2008). Glycerol is produced during biodiesel synthesis, and its availability is on the rise in parallel with increases in this renewable fuel’s production. The Blue Plains AWTP’s recent ENR upgrades included facilities allowing glycerol use; however, economics have favored continued use of CH₃OH.

   b. Proprietary renewable carbon substrates, which are marketed as replacements for CH₃OH; these are typically derived from agricultural crops or waste materials.

   c. Other readily degradable waste products from commercial or agricultural operations, which might be attractive if available near the WWTP. For example, REWA (Greenville, SC, USA) recovers off-specification vegetable and fruit products from a nearby industrial operation. They ferment the material to increase its degradability and use it as a biogenic denitrification carbon source.

2. **Sludge fermentation.** Readily degradable carbon can also be produced in a WWTP through fermentation of sludge; the fermented sludge streams are typically split into a lower-solids ‘fermentate’ and a concentrated solids phase. Fermentate can be fed to the denitrification process to satisfy carbon demand. Primary-sludge fermentation has been practiced at the Orange Water and Sewer Authority (OWASA in Chapel Hill, NC, USA) since 1990 (Brinch et al. 1994).
3. Reduced denitrification carbon demand through side-stream NO₂ pathways. Figure 6 provides an overview of the various NH₃-removal pathways currently used and/or under investigation (Shortcut Nitrogen Removal Task Force of the Water Environment Federation, 2015). Historically, facilities have used nitrification and denitrification pathways requiring the full addition of energy for O₂ supply and fully satisfying the carbon demand. Within the last 20 years, new processes have been developed that de-select for NO₂ oxidizing bacteria (NOB) and stop the oxidation processes at NO₂ (instead of NO₃), reducing aeration energy by 25% and carbon demand by 40%. This biological de-selection was originally accomplished with digester effluent by limiting O₂ concentrations and maintaining the process at higher temperatures, typically between 30 and 35 degrees C. These temperatures correlate nicely with anaerobic digester effluent as the process is typically operated at 35 degrees C (Van Hulle et al. 2006; Blackburne et al. 2008). These nitritation–denitritation processes have been used on digested sludge dewatering recycle streams and on the digested sludge itself (Parravicini et al. 2008). Other researchers have found that free nitrous acid can also be used to limit NOB activity (Wang et al. 2014).

4. Reduced denitrification carbon demand through side-stream deammonification. In many ways analogous to the NO₂ pathway, more WWTPs are now implementing processes using the deammonification pathway for sidestream treatment. Deammonification requires cultivation of anammox (anaerobic ammonium oxidation) archaea and NH₃ oxidizers through combinations of NO₂-pathway-like temperatures (for NOB de-selection), long biological detention times (35+ days) for anammox cultivation, and tightly controlled O₂ concentrations and pH (Van Loosdrecht & Salem 2006; Szatkowska et al. 2007). These processes convert half of the NH₃ to NO₂ and combine equal parts NO₂ and NH₃ to produce nitrogen gas while saving 62% of the energy and all of the carbon that would have been required by conventional nitrification–denitrification. DC Water’s deammonification upgrades are planned for start-up in 2017 and are expected to dramatically reduce the AWTP’s CH₃OH consumption.

A few less common options for reduced CH₃OH consumption include the following.

1. Ethanol. Most publicly traded, high-volume ethanol has been denatured to prevent human consumption but it is a readily available, renewable, carbon substrate that can be acquired for nominally more than CH₃OH (usually at a 5 to 20% premium). Fortunately for alternative carbon-sourcing and process suitability, ethanol is most typically denatured with CH₃OH (at approximately 5 to 10% of the total), making its Scope-1 anthropogenic GHG impact at least 90 percent lower than straight use of CH₃OH. If Scope-3 manufacturing emissions are additionally considered, ethanol production
the total of CH₃OH Scope-1 direct emissions of between 3.36 and 4.13 tonne CO₂e/tonne CH₃OH (for the Blue Plains ENR process, but dependent on solids disposition from non-destructive to full-carbon release) and Scope-3 manufacturing emissions of 0.67 tonne CO₂e/tonne CH₃OH (IPCC 2006a, 2006b) for a total ranging from 4.03 to 4.80 tonne CO₂e/tonne CH₃OH. Scope-3 emissions for today’s more-efficient corn-based-ethanol’s feed-crop production/farming, refining, and other product offsets (for products like corn and urea) are estimated to be 0.71, 0.73, and –0.42 tonne CO₂e/tonne ethanol respectively (converted from g/MJ at 25.2 MJ/kg ethanol; Liska et al. 2009) for an ethanol Scope-3 total of 1.02 tonne CO₂e/tonne ethanol. Based on Chen et al. (2015), the two alcohols have shown very similar per-unit-carbon process effectiveness in controlled laboratory tests so that direct comparison on the basis of fed carbon mass is appropriate. In summary, use of corn-based ethanol instead of CH₃OH would represent an emissions reduction of 90 to 95% for Scope-1 and 65 to 80% for Scope-1, -2 and -3 (as there is no difference in Scope-2 emissions).

2. Production of CH₃OH from digester gas. Tasher & Chandran (2015) are developing a process to biologically convert digester-gas CH₄ into CH₃OH using NH₃ oxidizers to replace fossil-fuel-derived CH₃OH. Vela et al. (2015) are researching the use of CH₄ as the electron donor (food source) for denitrification downstream of anaerobic treatment systems typically depleted of readily degradable carbon. Finally, although not likely practical when scaled for a WWTP, digester-gas CH₄ could be used as a feedstock to replace natural gas as a source for steam reforming or any other traditional CH₃OH manufacturing process.

3. Mainstream deammonification. More recently, researchers are trying to cultivate anammox in the liquid-treatment streams of WWTPs to enable treatment of raw-sewage NH₃ in addition to anaerobic-digestion sidestreams (Gilbert et al. 2015; Regmi et al. 2015). Mechanisms considered include producing anammox in sidestream treatment for bio-augmenting mainstream-treatment populations in combination with physically preventing anammox (with lower surface area, denser ‘granules’) from being discharged using cyclones, screens, or fixed-film growth on media trapped within the process by screens. These processes have the potential to completely eliminate the need for supplemental carbon in NH₃ treatment while dramatically reducing the WWTP’s total energy consumption and further reducing Scope-2 emissions from power consumption.

CONCLUSIONS

Once CH₃OH is added to a WWTP’s flow stream for denitrification, it is mostly released as CO₂, a conversion that occurs to a greater extent than that of other influent COD. This CO₂ is anthropogenic, yet has been overlooked by most GHG protocols until ICLEI’s recent update. CO₂ from CH₃OH is estimated to represent one quarter of all Scope-1 emissions from sewage treatment in the USA, an amount compounded by the fact that more plants and greater flows will be required to meet more stringent effluent total nitrogen standards, which will only increase CH₃OH use and its associated GHG significance over time. As a result, it is critical for WWTP operators, engineers, managers, and regulators to recognize that use of CH₃OH for process-carbon addition, while delivering specific environmental benefits, can significantly increase an operation’s GHG emissions.

The DC Water discussion demonstrates that CH₃OH CO₂ can be the most significant Scope-1 GHG source at a WWTP meeting stringent effluent nitrogen standards – even without anaerobic digestion of solids. Anaerobic digestion increases both the amount of CH₃OH needed and the fraction of CH₃OH-derived carbon released to the atmosphere as anthropogenic CO₂.

At the Blue Plains AWTP, solids-processing upgrades were implemented to achieve energy and operational cost savings, but have proven to also reduce the plant’s carbon footprint by over 33%. Relative changes to the 2012–2014 baseline emissions of 11,337 MT CO₂e/month after the upgrades were placed in service include the following:

- Increase of 9.3% (1,053 MT CO₂e/month) from increased Scope-1 CO₂ emissions
- Increase of 4.5% (513 MT CO₂e/month) from increased Scope-3 CH₃OH manufacturing emissions
- Decrease of 33.8% (3,833 MT CO₂e/month) from avoided Scope-2 electricity emissions
- Decrease of 13.5% (1,525 MT CO₂e/month) from avoided Scope-3 biosolids transport fuel and lime-manufacturing emissions
- Net result is 33.4% (3,792 MT CO₂e/month) overall GHG-emissions reduction post-digestion/CHP upgrades.

Once the deammonification process is brought on line in 2017, the following additional net improvements are projected, relative to the 11,337 MT CO₂e/month baseline:

- Decrease of 8.5% (970 MT CO₂e/month) from avoided Scope-1 CH₃OH CO₂ emissions

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For any business to create a near-50% GHG emissions reduction is quite significant. This reduction is especially significant when improvements are made through process upgrades versus simply purchasing wind or solar electricity generation. As a result of DC Water’s leadership, the quality of Blue Plains AWTP’s effluent and biosolids is improved and its carbon footprint reduced, while simultaneously reducing operating costs, achieving sustainable results on multiple levels and becoming an outstanding example for the rest of the industry.

Two directions for future research are recommended based on the findings herein:

1. Continued or accelerated research into alternative carbon sources or improved nitrogen removal processes like mainstream anammox with the added direct-GHG-emissions-reduction objective in addition to energy and cost savings.

2. Further research into other wastewater GHG emissions sources. These investigations should include both new reviews of existing protocols and methodologies that are poorly supported by science and new emissions sources that are altogether absent from today’s protocols. Willis et al. (2016) presents a number of opportunities for enhancing the scientific basis of the available GHG accounting protocols.

DC Water believes that improved understanding of its actual GHG emissions is important for obvious environmental reasons but for strategic purposes, as well. While not currently subject to GHG regulation, the utility anticipates eventually being subject to GHG-reduction requirements or some form of cap-and-trade program. Knowing what your actual emissions are is critical and foundational to identifying how you can and will address any new requirements, and not knowing represents a significant vulnerability. Identification and quantification of new emissions before regulators enact future GHG regulations is also important. Having a solid understanding of emissions sources can help to inform the baseline that regulators might set and how ‘new emissions’ sources are incorporated into GHG inventories.

ACKNOWLEDGEMENTS

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- Bill Brower maintains the DC Water GHG inventory, and organized and provided the background emissions data presented in this study.
- Christine DeBarbadillo led the start-up of the recent upgrades, and organized and provided the presented operational nitrogen-performance data and methanol use history.
- Sudhir Murthy, DC Water’s Innovation Officer, identified the anthropogenic methanol gap and assisted with development of ICLEI’s WW.9 methodology in 2011 while we served on the US Protocol’s Wastewater and Water Technical Advisory Committee.
- Ahmed Al-Omari assisted with the biomass yield calculations on both the COD and carbon bases.
- Chris Peot, DC Water’s Resource Recovery Director, helped develop DC Water’s GHG inventory template and data-mining software.

John Willis would also like to thank his long-time colleague and friend Bob Bastian with the EPA for suggesting consultation of EPA’s DMR database for the national significance section of this paper; Bob also provided review and input for the approximations that determined that 25% of national WWTP Scope-1 emissions are from CH₃OH CO₂.

Finally, Zhiguo Yuan, John Willis’s PhD advisor at The University of Queensland, provided critical guidance and review that made this paper much stronger; Dr Yuan also identified an error in an earlier version of the Blue-Plains-specific CH₃OH emissions factor that was fixed under his guidance.

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