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Title: Revisiting greenhouse gas mitigation from conventional activated sludge and anaerobic-based wastewater treatment systems

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Journal: Environmental Science: Water Research & Technology

DOI/Link: <https://doi.org/10.1039/C8EW00545A>

How to cite this post-print from LAUR:

Chen, S., Harb, M., Sinha, P., & Smith, A. L. (2018). Emerging investigators series: revisiting greenhouse gas mitigation from conventional activated sludge and anaerobic-based wastewater treatment systems. Environmental Science: Water Research & Technology, DOI: 10.1039/C8EW00545A, URI: <http://hdl.handle.net/10725/10168>

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Revisiting greenhouse gas mitigation from conventional activated sludge and anaerobic-based wastewater treatment systems

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Key words: methane, nitrous oxide, activated sludge, anaerobic processes, carbon footprint

1 Abstract

2 Recent literature on carbon dioxide (CO₂), methane (CH₄), and nitrous oxide (N₂O) emissions
3 from wastewater treatment plants (WWTPs) has highlighted the poor consensus in total
4 greenhouse gas (GHG) estimation (ranging from 0.243 to 2.4 kg CO_{2e}/m³). In the present study,
5 the major components of GHG emission variability in both conventional activated sludge (CAS)
6 and mainstream anaerobic WWTPs are systematically investigated as a basis for delineating a
7 roadmap to their future control and minimization. Through analysis of N₂O generation
8 pathways, it was determined that additional research via isotope labelling is necessary to
9 elucidate distinct generation mechanisms in CAS WWTPs (e.g., nitrifier denitrification and
10 hydroxylamine denitrification) and better predict N₂O contributions to total GHGs. Conversely,
11 mainstream anaerobic processes, although a potentially more sustainable alternative to
12 conventional aerobic treatment, introduce effluent dissolved CH₄ as a potentially significant GHG
13 contributor. Sweep gas and vacuum driven membrane contactors are promising dissolved
14 methane management strategies. However, further optimization of gas-to-liquid ratios and
15 transmembrane pressures, respectively, are vital to balancing treatment efficiency with energy
16 neutral/positive operation. Overall, a thorough elucidation of N₂O generation pathways in CAS
17 WWTPs and the development of effective dissolved CH₄ management strategies for mainstream
18 anaerobic processes will define their respective future roles in reducing wastewater-associated
19 GHG emissions.

20 Water Impact

21 Conventional and mainstream anaerobic wastewater processes remain difficult to compare in
22 terms of their global warming potential (GWP) due to unresolved variability in high-impact GHG

23 emissions. Here, we identify knowledge gaps in those GHG contributors, highlight potential
24 mitigation strategies, and provide a basis for the direct comparison of CAS and anaerobic
25 wastewater treatment.

26 1. Introduction

27 As the risks of climate change become increasingly acute, the necessity for accurate greenhouse
28 gas (GHG) accounting has led to a renewed focus on wastewater management as a GHG
29 emissions source. The most widely employed wastewater treatment methods, namely aerobic
30 (i.e., activated sludge-based processes) and mainstream anaerobic processes, both significantly
31 contribute to GHG generation in their current forms of implementation. The most recently
32 completed EPA Inventory of GHG Emissions and Sinks estimated that US wastewater treatment
33 plants (WWTPs) accounted for approximately 0.3% of overall emissions in 2016, with CH₄ and
34 N₂O accounting for 3 and 5 MMT CO₂ equivalents, respectively.¹ CH₄ and N₂O are of particular
35 concern due to their relatively high 100-year global warming potentials (34 and 298 CO_{2eq},
36 respectively).² WWTPs are currently estimated to be the sixth largest contributor to N₂O
37 emissions worldwide (approximately 3%).³ GHG emission uncertainty in WWTPs is largely
38 derived from N₂O given the gaps in our understanding of formation mechanisms and the overall
39 magnitude of emissions.^{4,5} Mainstream anaerobic processes are receiving renewed interest as
40 an alternative to aerobic processes due to their potential to lessen WWTP energy costs and
41 biosolids generation.⁶ Yet, a direct comparison of GHG emissions between aerobic and
42 anaerobic processes remains lacking and is needed information to navigate a potential
43 transition to anaerobic treatment.

44 Today, conventional activated sludge (CAS) processes coupled with anaerobic digestion are
45 widely used in domestic wastewater treatment, despite their high energy requirements (up to

46 3% of overall US electricity consumption) and lack of large-scale energy and nutrient recovery.⁷
47 Although anaerobic digestion significantly offsets WWTP energy demands and reduces sludge
48 handling requirements, it is unclear whether this conventional approach will remain attractive in
49 light of recent advances in mainstream anaerobic treatment.⁸ Mainstream anaerobic systems
50 directly recover energy via biogas production, produce drastically less sludge, and have been
51 proven viable at a range of operational temperatures.⁹ However, loss of dissolved CH₄ in
52 effluents is an outstanding concern. Such losses not only reduce energy recovery, but also pose
53 severe environmental impacts due to GHG emissions.⁶

54 Several review papers have been published to address GHG emissions from conventional
55 WWTPs, many of which have focused specifically on N₂O emissions.^{4, 10-12} For mainstream
56 anaerobic treatment, a recent review by Crone et al. evaluated dissolved effluent CH₄ while
57 discussing technologies for recovery.¹³ Despite the significant contributions of the
58 aforementioned reviews, N₂O and CH₄ emission quantifications for the purpose of directly
59 comparing CAS and mainstream anaerobic treatment systems' GWP remain unavailable. The
60 primary purpose of the current study is to systematically focus on outstanding knowledge gaps
61 in GHG emissions limiting direct comparability of CAS and mainstream anaerobic treatment. The
62 issues specifically evaluated in this work include CAS WWTP total GHG estimation, pathway-
63 associated N₂O generation mechanisms in aerobic-based WWTPs, and dissolved CH₄ recovery
64 efficiency for anaerobic system effluents.

65 2. Anthropogenic GHG emissions from CAS WWTPs

66 2.1. Overview of GHG generation in wastewater treatment processes

67 GHG emissions are attributable to essentially every unit process in conventional aerobic
68 wastewater treatment coupled with anaerobic digestion (Figure 1). Here, we categorize these

69 emissions as either direct or indirect, where direct emissions include GHGs physically produced
70 by either in-plant or downstream environmental processes and where indirect emissions include
71 electrical energy demands and chemical inputs of the system. From the perspective of indirect
72 emissions, aeration tanks comprise more than 40% of total plant energy demand^{7, 14, 15} and are
73 often reported as contributing most significantly to overall GHG emissions (approximately 0.298
74 kg CO_{2e}/m³ based on reported U.S. energy carbon footprint of 0.472 kg CO₂/kWh).¹⁶⁻¹⁹

75 Sidestream processes for primary and waste activated sludges also contribute indirect GHG
76 emissions via energy demand and chemical addition during dewatering, transportation, land
77 application, and landfilling,^{20, 21} which can account for between 0.134 to 0.167 kgCO_{2e}/ m³ of
78 domestic wastewater.²² It should be noted, however, that biogas production from anaerobic
79 digestion can significantly offset indirect GHG emissions by lessening reliance on a potentially
80 GHG emission heavy primary energy mix.^{18, 20}

81 Regarding direct GHG emissions, N₂O generated during denitrification, either in anoxic tanks (in
82 the case of CAS with biological nitrogen removal) or in the receiving aquatic environment when
83 nitrate-rich effluent is released (in the absence of on-site anoxic treatment), is considered the
84 primary source of direct GHG emissions.¹ It should be noted that the EPA's Inventory of US
85 Greenhouse Gases and Sinks reports this N₂O emission source as part of effluent emissions due
86 to the majority of plants not employing biological nitrogen removal. However, in scenarios
87 where nitrogen removal is achieved, these emissions are largely confined to within the plant
88 footprint.²³ Aeration tanks are also responsible for direct N₂O generation as a result of
89 incomplete nitrification, with their contribution to total N₂O footprint being recently identified
90 as potentially much higher than previously considered.¹ In addition to N₂O, aeration tanks are
91 also responsible for significant generation of CO₂ due to microbial degradation of organic
92 carbon, however, these direct CO₂ emissions are not traditionally considered in GHG accounting

93 because of their biogenic origin.²⁴ Despite this, recent research has shown that approximately
94 14% of total organic carbon in municipal wastewater is actually of non-biogenic origins due to
95 domestic use of soaps and detergents, leading to an underestimation of direct GHG emissions.²⁵
96 ²⁶ Quantifying direct emissions of CAS WWTPs has proven to be the most challenging aspect of
97 GHG estimation, as quantification methods and assumptions are wide ranging in existing
98 literature and governmental reports. In the following, GHG emissions are normalized to volume
99 of domestic wastewater (DWW) treated to better compare parallel studies, regardless of
100 differences in treatment process.

101 2.2. Common findings of different quantification methods for plant-wide GHG 102 emissions

103 Two common approaches have been reported for quantifying direct GHG emissions: (1)
104 emission factor-based methods derived from dynamic modeling and (2) actual emission values
105 determined from on-site measurement. Generally, model-based studies have reported high
106 variability in overall plant emissions (from 0.24 to 2.4 kg CO_{2e}/m³ DWW), with contradictory
107 findings regarding the primary source of emissions.^{14, 27-29} A clear consensus has thus not yet
108 been reached identifying the major contributors to total GHG emissions.⁵ Models are typically
109 constrained to specific plant configurations and feature inconsistent emission factors.
110 Nonetheless, one common observation is that N₂O emissions contribute the greatest
111 uncertainty in emissions estimation,^{27, 30} particularly due to its excessive GWP and the lack of a
112 comprehensive mechanism-based model of formation.⁵

113 On-site quantification methods have included sampling and subsequent lab analysis,^{16, 17, 31} on-
114 line off-gas collection and analysis,³²⁻³⁵ and tracer dispersion monitoring.³⁶ Normalization of on-
115 site sampling methodology has enabled the comparison of different treatment processes, such

116 as activated sludge, oxidation ditches, anaerobic/anoxic/aerobic processes (A²O), and reverse
117 A²O.^{16, 31} Research taking advantage of covered treatment units and direct off-gas on-line
118 analyzers showed correlation between operational conditions and GHG emissions. Such trends
119 include emission increases with seasonal water temperature variation,³² changes in aeration
120 rates,³³ discharge of reject water to influent streams,³³ length of anoxic/oxic phases (in
121 sequencing batch reactors (SBRs)),³⁴ and influent nitrite variations.³⁵ The use of less
122 conventional approaches, such as tracer addition and dispersion monitoring, have generally
123 been less accurate compared to on-site measurement. A study by Yoshida et al., for example,
124 that utilized tracers and mobile cavity ring-down spectroscopy sampling, found large variations
125 in emissions over multiple campaigns, with CH₄ generation ranging from 4.99 to 92.3 kg/h and
126 N₂O from 0.37 to 10.5 kg/h.³⁶

127 Although aeration energy consumption is the primary contributor to indirect GHG emissions,^{27,}
128 ^{32, 34} direct emission rates remain less clear and are a significant obstacle to achieving a plant-
129 wide understanding.^{16, 17, 31} Further, aeration control strategies impact both energy consumption
130 and N₂O generation (affected by DO levels), implying that tradeoffs exist between direct and
131 indirect GHG emissions.¹⁴ Existing literature has reported between 0 and 14.6% of nitrogen
132 entering WWTPs being converted to N₂O,^{4, 20, 22, 34, 36} contributing 1% to 78.4% of overall plant
133 carbon footprints.^{17, 18, 22, 32, 34} Based on this extreme variability, a more thorough evaluation of
134 literature addressing N₂O emissions in aerobic-based WWTPs is necessary.

135 2.3. Specific direct GHG emission sources in CAS WWTPs

136 2.3.1. Considering total CH₄ emissions

137 Unintentional methanogenic conditions in collections systems, influent piping, grit chambers,
138 primary clarifiers, and anoxic/oxic tank dead zones all contribute to methane-based GHGs.^{18, 37, 38}

139 Existing studies have shown that this upstream-generated CH₄ is predominantly stripped from
140 the liquid phase upon reaching the aeration tanks, serving as the primary source of CH₄
141 emissions in the mainstream portion of WWTPs (6-18 g CO_{2e}/m³ DWW).³⁹⁻⁴³ Further, the low
142 organic carbon and high DO remaining in solution after aeration minimize the potential for any
143 additional evolution and release of CH₄ in WWTP effluents (reportedly <0.1% of total CH₄
144 emissions).⁴⁴

145 Only a few studies on GHG emissions have incorporated sidestream anaerobic digestion. Two
146 studies by Daelman et al.^{32, 45} reported total methane-associated emissions in the range of 90-95
147 g CO_{2e}/m³ DWW, showing that fugitive gasses associated with sludge handling, digester
148 effluents, and cogeneration engine gas slip accounted for approximately three quarters (72 ±
149 23%) of WWTP CH₄ emissions. An analysis of studies reporting total digester CH₄ emissions
150 (ranging from 17 to 72 g CO_{2e}/m³ DWW) suggested that operational parameters such as WWTP
151 SRT and anaerobic digester residence time likely play a significant role in CH₄ emission rates.⁴⁶
152 Digestion associated CH₄ losses, if fully recovered, could potentially increase energy recovery by
153 10-30%.²⁰ These results imply that although CH₄ is a relatively minor component of direct CAS
154 emissions, reducing their losses in sludge treatment processes can significantly improve energy-
155 associated GHG footprints.

156 2.3.2. N₂O emissions: taking generation pathways into account

157 N₂O generated during biological nutrient removal is one of the most variably reported
158 phenomena known to occur in conventional WWTPs. The current US EPA guidance on national
159 GHG inventories estimates that 0.5% of influent nitrogen will be converted to N₂O, primarily due
160 to denitrification of effluent nitrate in receiving waterways.^{24, 47} This emission factor was
161 originally developed as part of a study by Czepiel et al. that did not include in-plant

162 denitrification.⁴⁸ More recent work on N₂O emissions from full-scale wastewater treatment
163 systems, however, have reported values ranging from 0 to 14.6% of N. To elucidate source
164 variability, a fundamental understanding of the factors affecting N₂O generation is necessary.

165 In CAS-based treatment, ammonium-containing wastewater is intentionally subjected to aerobic
166 and anoxic conditions to convert nitrogen to dinitrogen gas via nitrification and denitrification.
167 However, this process also has potential to contribute N₂O emissions through multiple distinct
168 and complex pathways (Figure 2). When autotrophic ammonium oxidizing bacteria (AOB) are
169 present at low DO, high nitrite, or high ammonium conditions, AOB will perform denitrification,
170 converting nitrite to N₂O (also known as nitrifier denitrification).⁴⁹ Nitrite can also independently
171 react with coexisting organic or inorganic matter during the nitrification process to produce N₂O.

172 Another intermediate during ammonium oxidation, known as a nitrosyl radical, has also been
173 observed to convert to N₂O, either biologically or chemically.⁵⁰ During the denitrification
174 process, N₂O serves as a necessary intermediate and will accumulate as a result of oxygen
175 intrusion into the anoxic environment, high nitrite concentrations, or limited carbon source
176 availability. The cause of this accumulation is most commonly the inhibition of N₂O reductase. In
177 other cases, the presence of a hydroxylamine intermediate during ammonium oxidizing
178 conditions can promote N₂O generation through alternative pathways. This reaction can
179 proceed with either oxygen as the electron acceptor (hydroxylamine oxidation) or with nitrite as
180 the electron donor (N-nitrosation).

181 Although nitrifier and heterotrophic denitrification are considered the two main sources of N₂O,
182 other less understood pathways likely play a significant role.⁵¹⁻⁵³ Recent studies have added
183 inhibitors such as allylthiourea and chlorate to accredit N₂O emissions to nitrifier denitrification,
184 heterotrophic denitrification, or NH₂OH oxidation pathways.^{51, 54, 55} An underlying problem with
185 this approach, however, is that these inhibitors also inhibit nitrification, in addition to the

186 processes that generate N₂O via nitrifier denitrification. A promising alternative for N₂O
187 emission source differentiation with high resolution is labelled isotope-based nitrogen species
188 introduction and tracking.⁵⁶

189 2.3.3. Operational factors affecting N₂O emissions

190 Environmental conditions, operational parameters, wastewater characteristics, and varying
191 WWTP configurations can (individually or collectively) induce and/or increase N₂O generation.
192 Further, numerous N₂O formation pathways have been identified across a range of microbially
193 selective environments. Elucidating relationships between these variables and known N₂O
194 generation mechanisms remains challenging. In the following, a critical analysis of the potential
195 relationships between these two areas of literature is provided.

196 2.3.3.1. Dissolved oxygen control

197 Multiple reviews focusing on N₂O emissions from WWTPs have concluded that DO levels are
198 primarily responsible for its generation—low DO during nitrification and high DO during
199 denitrification.⁴ However, existing literature that has investigated N₂O formation during partial
200 and/or full nitrification has reached contradictory conclusions regarding the role of DO. For
201 example, multiple studies on pure culture,^{55, 57} batch experiments,^{51, 58} lab-scale reactors (SBR
202 and CSTR),⁵⁹⁻⁶³ and pilot/full-scale wastewater treatment plants^{62, 64} have observed higher
203 emissions at low DO conditions during nitrification. In most of these studies, the accumulation
204 of NO₂⁻ was closely related to high N₂O emissions at low aeration rates. Conversely, other pure
205 culture studies,^{65, 66} lab-scale experiments^{54, 67-69}, and a full-scale nitrification-anammox reactor
206 investigation^{70, 71} have found elevated N₂O emissions under higher DO conditions. It is likely that
207 these varying observations result from differences in microbial community structure and activity
208 profiles leading to distinctly different formation mechanisms.

209 Recent studies have used nitrification inhibitor addition and/or isotope labelling of N-species to
210 pair N₂O emissions with their specific generation pathways at varying DO levels. The use of
211 nitrification inhibitors, specifically, has revealed decreasing relative contributions of AOB
212 denitrification,^{51, 58} increasing NH₂OH oxidation contributions, and constant heterotrophic
213 denitrification contributions to overall N₂O emissions at increasing DO.⁵⁴ Further insight
214 provided in a study by Peng et al.,⁶⁸ which used isotopic site preference measurements, showed
215 increases in NH₂OH oxidation-sourced N₂O and decreases in AOB denitrification-induced
216 emissions with rising DO (from 0.2 to 3 mg/L). Based on the cumulative findings of these
217 studies, it can be concluded that although AOB denitrification is commonly the dominant N₂O
218 production pathway, the NH₂OH oxidation pathway could outcompete at high DO (e.g., 3.5 mg
219 O₂/L) when combined with low NO₂⁻ (e.g., <10 mg O₂/L).⁵⁸ Ultimately, more applied research
220 quantifying both gaseous and aqueous N₂O is needed, while taking into consideration all
221 possible N₂O generation pathways.

222 2.3.3.2. pH

223 Studies investigating N₂O emissions during nitrification at different pH ranges have generally
224 observed highest production at pH 8-8.5, independent of free ammonia and nitrous acid
225 concentrations.^{55, 72} N₂O emissions during denitrification have been conversely observed to
226 decrease with increasing pH across 5-8.5, with concurrent decreases in NO₂⁻.⁷³⁻⁷⁵ One study
227 specifically found that no N₂O formation was detected at pH >6.8 and highest production
228 occurred between 5 and 6.⁷⁴ Nonetheless, given that free nitrous acid is believed to exert a
229 stronger inhibitory effect on N₂O reductase than pH and has been strongly correlated with N₂O
230 production, it is possible that the relationship between pH and N₂O production during
231 denitrification is purely incidental.⁷⁵

232 2.3.3.3. Nitrite

233 In addition to its oxidation by O_2 , NH_2OH can also serve as a precursor to N_2O formation via its
234 reaction with nitrite (known as N-nitrosation). Even when NH_2OH is present as an intermediate
235 in the ammonium oxidation process at low concentrations, the N-nitrosation hybrid reaction has
236 still been observed to proceed in full-scale bioreactors (0.03 to 0.11 mg N/L).⁷⁶ Isotope labelled
237 $N^{15}O_2^-$ and $N^{15}H_2OH$ have been used to distinguish respective contributions of nitrifier
238 denitrification, the N-nitrosation hybrid reaction, and NH_2OH oxidation in a partial nitrifying
239 bioreactor.⁵⁶ The N-nitrosation reaction was the prominent formation pathway in this study,
240 possibly due to the relatively high DO levels. These results imply that high nitrite concentrations
241 can result in significant N_2O formation in the nitrification process, even in the absence of nitrifier
242 denitrification.

243 Increasing nitrite concentrations during denitrification have also been observed to limit the
244 generation of NO reductase, leading to accumulation of nitric oxide (NO).⁷⁷ This can further
245 impact N_2O emissions, as NO causes an inhibitory effect on enzymes involved in the
246 denitrification process (e.g., nitric acid and N_2O reductases). In a mixed microbial community of
247 both nitrifiers and denitrifiers, for example, Tallec et al.⁵¹ observed up to an eight fold increase
248 in N_2O production with nitrite addition at 1 mg O_2/L . Further, specific tests on oxidized nitrogen
249 in an aerobic granule sludge system have shown specific N_2O generation to be approximately
250 44% higher in the presence of nitrite as compared to nitrate alone.⁵⁹ Although the mechanisms
251 of N_2O formation in nitrification and denitrification processes are distinctly different, nitrite
252 presence plays a significant role in both.

253 2.3.3.4. Carbon source availability/COD:N ratio

254 As has been reviewed,^{4, 10, 11} limited availability of carbon sources increases N₂O production
255 during denitrification. Although the exact mechanism by which this occurs is not fully
256 understood, competition for electrons between various denitrification enzymes (i.e., NO₃⁻, NO₂⁻,
257 NO and N₂O reductase) is likely the cause.¹¹ Specifically, NO₃⁻ and NO₂⁻ reductases have
258 relatively higher electron affinity than NO reductase and N₂O reductases, which induces
259 incomplete denitrification under carbon limited conditions. Increased N₂O production in carbon
260 source-limited environments can also be due to microbial consumption of internal storage
261 compounds (i.e., poly-β-hydroxybutyrate (PHB)).^{4, 11} In simultaneous nitrification/denitrification
262 and phosphorus removal processes employing denitrifying phosphate accumulating organisms
263 (DPAOs), N₂O generation has been observed to start immediately after the pulse addition of
264 nitrite,⁷⁸ but further research is needed to determine the intrinsic mechanism of this
265 phenomenon.

266 To maintain the minimum COD:N ratio necessary to accomplish full denitrification (typically
267 considered to be > 4), the addition of external substrate as a carbon source is often required.¹¹
268 This practice has been shown in certain instances to also significantly reduce N₂O production (by
269 up to 95%).⁶⁹ As such, a range of external carbon source/substrate types (e.g., acetate,
270 methanol, mannitol, glucose, starch, acetic acid, sludge fermentation liquid) have been
271 investigated for their effectiveness at curbing N₂O formation.^{69, 79-82} Resultantly, distinctive
272 changes in both microbial diversity and N₂O production rates have been observed with different
273 substrates. These differing microbial communities, which exert preferential consumption of
274 each carbon source type, will ultimately dictate the enzymatic activity responsible for both NO
275 and N₂O reduction.

276 2.3.3.5. Ammonium shock

277 Returning ammonium-rich reject water to the headworks can significantly contribute to N₂O
278 emissions due to ammonium shock, especially during downstream transitions from anoxic to
279 aerobic conditions/environments.^{66, 70} Given that this transition in redox conditions is often
280 unavoidable, the accumulation of ammonium in anoxic environments should be closely
281 monitored. Ammonium shock can also induce decreases in DO levels, potentially triggering
282 nitrifier denitrification and subsequent elevated N₂O emissions.⁸³ Lab-scale work investigating
283 this phenomenon has identified a critical ammonium loading rate of approximately 1.60 mg
284 NH₃-N/g TSS, beyond which nitrite and N₂O increase significantly.⁸⁴

285 2.3.4. Implications of N₂O emissions in CAS WWTPs

286 Optimization of key operational parameters (i.e., sufficient carbon sourcing, pH, DO, and
287 ammonium levels) is key to achieving predictable and minimized N₂O emission rates. A
288 challenge associated with plant-level N₂O source identification is that nearly all N₂O is emitted
289 from aeration tanks, regardless of formation pathway.^{64, 85} Therefore, more research employing
290 isotope labelling is likely necessary to elucidate the underlying mechanisms and their
291 contributions to overall N₂O emissions. With a better understanding of each N₂O generation
292 pathway and its role within treatment systems, specific strategies can be devised to mitigate
293 N₂O emissions and ultimately standardize operational guidelines to reduce nationwide GHG
294 emissions.

295 3. GHG emission management for mainstream anaerobic

296 treatment

297 Anaerobic processes are considered a sustainable and energetically favorable alternative to
298 conventional aerobic processes. Anaerobic processes directly convert organics to methane-rich
299 biogas and eliminate energy requirements associated with aeration.⁹ Taking advantage of their
300 favorably warm climate, several Latin American countries have long incorporated mainstream
301 anaerobic processes, specifically upflow anaerobic sludge blankets (UASBs), for full-scale
302 domestic wastewater management.^{86, 87} The integration of membrane separation and anaerobic
303 treatment (i.e., anaerobic membrane bioreactors (AnMBRs)) has greatly expanded interest in
304 mainstream anaerobic processes worldwide.^{88, 89} This has led to recent advances in the
305 technology's application at ambient temperatures, as well as promising testing at the pilot-
306 scale.^{90, 91} However, the release of dissolved CH₄ along with discharged effluents remains a
307 significant implementation concern, severely increasing GHG emissions while concomitantly
308 reducing potential energy recovery.^{6, 13} Such losses, which in extreme cases account for up to
309 90% of total produced CH₄, pose a severe environmental threat if mainstream anaerobic
310 treatment becomes the norm.⁸⁷ However, successful mitigation of these emissions would enable
311 anaerobic treatment with less GHGs than CAS processes, providing impetus for advancing
312 dissolved CH₄ recovery technologies.⁹²

313 3.1. GHG emission sources in anaerobic bioreactors

314 Given that the majority of GHG emission-related research on anaerobic treatment has been
315 conducted at the bench- and pilot-scale,⁹³⁻¹⁰⁶ full-scale indirect CO₂-based emissions estimates
316 for electricity consumption remain largely unconfirmed. Nonetheless, energy balances of
317 mainstream anaerobic treatment are generally expected to significantly improve upon current

318 CAS.¹⁰⁷ In addition, an objective comparison of GHG emissions between CAS and mainstream
319 anaerobic processes requires inclusion of downstream nutrient removal processes for anaerobic
320 systems (e.g., partial nitrification-anammox). Such nitrogen removal processes have been shown
321 to emit even higher levels of N₂O than CAS, as reviewed by Massara et al.,¹⁰ and necessitate
322 further process optimization to be successfully mitigated.

323 Even accounting for these uncertainties, the most significant GHG-associated threat from
324 mainstream anaerobic treatment remains effluent CH₄ losses. CH₄ saturation relative to Henry's
325 Law in anaerobic effluents has been observed to range between a factor of 1.0 to 5.2, resulting
326 in the loss of 10-90% of total CH₄ produced.¹³ Recent work has demonstrated robust operation
327 (i.e., COD removal) at temperatures as low as 6°C. However, such low temperatures exacerbate
328 GHG emission concerns by inherently increasing CH₄ solubility.⁹⁶ Overall, CH₄ solubility at low
329 temperatures is largely responsible for increasing trends in dissolved CH₄ concentrations across
330 all anaerobic bioreactor system types (Figure 3a), despite reactor configuration and biogas
331 composition also playing a role. Although the integration of membrane filtration in AnMBRs has
332 improved effluent quality at such low temperatures, similar CH₄ oversaturation is still
333 observed.^{101, 106} Studies by Smith et al.^{106, 108} on low-temperature AnMBR operation, specifically,
334 have documented the likelihood that high methanogenic activity in membrane biofilms are
335 responsible for dissolved CH₄ oversaturation. Experimental findings suggested that as systems
336 increasingly relied on membrane biofilm-based treatment at decreased temperatures, biofilm
337 methanogens directly emitted CH₄ into the effluent.¹⁰⁶

338 Although limitations of gas-liquid transfer rates have been identified as an obstacle for recovery,
339 *in-situ* biogas sparging readily achieves gas-liquid equilibrium and maximizes CH₄ evolution to
340 headspace. Several recent studies have demonstrated effluent CH₄ saturation factors of close to
341 1 and/or reduced dissolved CH₄ content by up to 50% by employing *in-situ* biogas sparging.^{98, 103}

342 AnMBRs operating at temperatures above 20°C have also shown relatively low saturation
343 factors (in the range of 1.0 to 1.1).^{100, 109, 110} Yet, other work has shown CH₄ saturation exceeding
344 a factor of 1.5 or greater, even when biogas sparging is sufficiently utilized.

345 The strongest deviation above CH₄ saturation level was observed for scenarios at 15°C and lower
346 (Figure 3b). In some scenarios, no biogas CH₄ was produced, with all produced CH₄ being
347 evolved in the effluents (Figure 3c).^{96, 106} Given that this phenomenon is likely caused by
348 disproportionate biofilm-based CH₄ production, it cannot be easily mitigated by reactor biogas
349 sparging/stripping.^{101, 106} Using 34 as a standard GWP factor for CH₄, GHG emissions from
350 dissolved CH₄ were calculated to be in the range of 0.281 to 2.82 kg CO_{2e}/m³ DWW. This is
351 generally comparable to the wide-ranging rates of CAS (0.24 to 2.4 kg CO_{2e}/m³) and will
352 ultimately necessitate downstream CH₄ recovery technologies.

353 3.2. Utilizing membrane contactors for dissolved CH₄ recovery

354 Of the physiochemical-driven methods examined for dissolved CH₄ removal and/or recovery
355 from anaerobic effluents, the most widely tested involves membrane contactors for effluent CH₄
356 desorption. Relevant operational parameters of these systems include membrane properties,
357 contact area, gas/liquid flow rates, flow direction, vacuum pressure, and gas/liquid supply
358 sources (shell or lumen). In the following, we provide a comparative analysis of the energy
359 use/recovery potential of the two primary modes of membrane contactor operation, namely
360 sweep gas- and vacuum-based desorption.

361 3.2.1. Sweep gas membrane contactors

362 When operating membrane contactors in sweep gas mode, dissolved CH₄ removal in the liquid
363 phase is driven by a concentration gradient across a gas permeable membrane into crossflowing
364 nitrogen or air. Several studies have successfully demonstrated dissolved effluent CH₄ removal

365 rates from UASB, AnMBR, and synthetic effluents of up to 98.9% and 92.6% using microporous
366 and nonporous hollow fiber membrane contactors (HFMCs), respectively.^{110, 111} The
367 aforementioned studies employed polydimethylsiloxane (PDMS) membranes (both microporous
368 and nonporous types). Another recent study utilized fluorinated silica nanoparticle modified
369 membranes to enhance surface hydrophobicity.¹¹² These modified membranes attained higher
370 CH₄ recovery fluxes as compared to a commercial polypropylene microporous membranes (400-
371 550 mg CH₄/m²·h vs. 200-350 mg CH₄/m²·h) over 300 h of operation, implying that such surface
372 modifications can alleviate long-term pore wetting issues.

373 3.2.2. Vacuum suction (degassing) membrane contactors

374 Membrane contactors operated in vacuum mode rely primarily on a pressure differential
375 without significant gas cross-flow to achieve high-concentration CH₄ recovery. This allows for
376 the direct use of captured CH₄ without further purification, but also requires additional energy
377 input in the form of vacuum pressure. Multiple early studies by Bandara et al.^{94, 96, 113} on
378 membrane degasification for UASB effluents using a commercial multi-layer composite
379 polyethylene hollow-fiber membrane contactor (HFMC) successfully desorbed 77% to 86% of
380 dissolved CH₄ from UASB effluents into the lumen at vacuum pressures of 50 and 80 kPa.⁹⁴
381 Lumen-side liquid flow (as opposed to shell-side), has generally been observed as more effective
382 at CH₄ desorption due to superior liquid to air transfer rates, however it can be limited by hollow
383 fiber flow-path clogging over long-term operation.^{13, 114}

384 3.3. Analysis of energy demands and recovery by membrane contactors

385 Superior removal rates are achievable by vacuum degasification as compared to sweep gas
386 operation.¹¹⁵ Further, vacuum desorption has specific advantages associated with direct on-site
387 CH₄ use, which are not achievable by sweep gas contactors. Such advantages, however, must be

388 evaluated in comparison with the greater energy requirements of vacuum-driven
389 transmembrane pressure (TMP). Given the knowledge gaps in literature from the perspective of
390 energy use and recovery, a comparative analysis of the practical limitations of each CH₄ recovery
391 method is necessary to assess each technology's economic feasibility and overall GWP.

392 As summarized in Table 1, CH₄ concentrations for sweep gas driven membrane contactors are
393 generally less than 2.4% of total off-gas volume, with only one case demonstrating relatively
394 high concentrations of 23.2% with a polypropylene HFMC operated at low gas to liquid (G/L)
395 ratios.^{97, 110-112, 114-116} In most cases, sweep gas driven membrane contactors exhibited increasing
396 effluent removal efficiencies at higher gas to liquid (G/L) ratios, which also lead to decreased
397 CH₄ off-gas purity. The majority of studies to date investigating sweep gas membrane contactor
398 use have had a primary objective of reducing effluent concentrations to eliminate combustion
399 risks in downstream discharge piping. Therefore, the systems were not operated to achieve
400 optimal off gas concentrations. Without post-removal purification of sweep gas, limited
401 approaches are available for utilization, as CH₄ concentrations are generally too low for even
402 basic off-gas flaring (i.e., >5% CH₄). However, recent developments have shown that direct
403 combustion via thermal/catalytic flow reversal reactors, regenerative/catalytic oxidation, or lean
404 burn-gas turbine combustion can be achieved at CH₄ concentrations as low as 1%.¹¹⁷
405 Implementing such air-based off-gas in on-site cogeneration plant engines has been proposed
406 previously for anaerobic digester dewatering process gasses.⁴⁵ These applications, in
407 combination with optimization of G/L ratios, could lead to sweep gas membrane contactors
408 being a viable option for effluent CH₄ GHG mitigation.

409 A recent review by Crone et al.¹³ calculated an energy input to recovery ratio of 1.0 for effluent
410 CH₄ recovery using vacuum driven membrane contactors. However, given the high variability in
411 existing literature associated with operational parameters of vacuum degasification, a more

412 comparable evaluation of these variables is necessary. Table 2 provides a normalized summary
413 of studies on vacuum-driven membrane contactors, their energy requirements, and the
414 potential energy content of recovered CH₄ using a unified methodology. Results of multiple
415 studies suggest that systems operated at TMPs between 14 and 50 kPa are generally energy
416 positive while maintaining CH₄ recovery rates between 60 and 90%.^{94, 113-115} Further, CH₄
417 recovery in different scenarios did not improve substantially with increasing vacuum pressure,
418 proving that low vacuum scenarios are generally effective. Based on these observations,
419 operating vacuum driven membrane contactors at relatively low vacuum pressures (< 50 kPa)
420 can enable the entire HFMC system to be energy neutral/positive while achieving sufficient
421 effluent GHG reduction.

422 3.4. Biological approaches

423 Biological oxidation is a promising alternative strategy for CH₄ removal from anaerobic effluents.
424 The most common technique is the downflow hanging sponge (DHS). This method has proven
425 highly effective by numerous studies, as previously reviewed.¹³ In comparison, another
426 potentially promising treatment system that has yet to be fully investigated is known as
427 denitrifying anaerobic CH₄ oxidation (DAMO), and is reviewed herein.

428 3.4.1. Effective CH₄ removal by the downflow hanging sponge (DHS)

429 Several recent studies have utilized DHS bioreactors for the aerobic oxidation of dissolved CH₄
430 with relatively consistent removal results^{105, 118-120}. Through the optimization of operational
431 parameters such as wastewater composition and air flowrates, systems have achieved removal
432 of multiple residuals (e.g., CH₄, ammonium, sulfur, etc.). While some have employed varying
433 HRTs and aeration rates to achieve removals of up to 97% of dissolved CH₄ using single stage
434 DHS reactors,¹¹⁸ other work has shown that two-stage DHS systems are capable of both

435 recovering CH₄ in off-gas at high concentrations (>30%) and oxidizing the remaining content to
436 achieve near complete removal of dissolved CH₄ (>99%) from effluents.¹¹⁹ Air flowrate is a
437 critical operational parameter, as varying oxygen affinity and growth rates among different
438 microbial communities significantly affect removal.¹²⁰

439 3.4.2. The case for denitrifying anaerobic CH₄ oxidation (DAMO)

440 A more recently proposed method, known as DAMO, provides a potential solution for CH₄
441 removal through its use as an electron donor. DAMO archaea are capable of reducing nitrate to
442 nitrite while DAMO bacteria convert nitrite to nitrogen gas. Combining DAMO and anammox
443 has recently been proposed as a means for simultaneous nitrogen and CH₄ removal from
444 anaerobic effluents.¹²¹ Nitrate reduction by DAMO archaea and nitrite reduction by DAMO
445 bacteria with CH₄ oxidation are achieved through the sequential CH₄ oxidation processes below,



448 while nitrite reduction/ammonium oxidation by anammox concurrently produces nitrate:



450 Recent studies by Chen et al.^{122, 123} have developed a system based on this model using a
451 membrane biofilm reactor (MBfR). Multiple lab-scale investigations have shown that biofilms
452 containing cocultures of DAMO and anammox microorganisms can achieve sufficient nitrate and
453 nitrite reduction and ammonia oxidation.^{124, 125} Ultimately, the application of a combined
454 anammox and DAMO process could offer significant economic and practical advantages over
455 conventional practices if successfully combined with anaerobic systems. The implementation of
456 this process for treatment of anaerobic bioreactor effluents, however, is highly dependent on

457 the co-enrichment of specific DAMO and anammox organisms and the supplementation of
458 nitrite to the system. Although magnetically stirred gas lift reactors (MSGLRs), MBfRs, and
459 granular sludge reactors have all been identified as capable of supporting growth of DAMO
460 microorganisms and retaining biomass effectively,^{122-124, 126-129} the most feasible option thus far
461 for integration of anammox and DAMO is MBfRs.

462 Although such applications are still in their infancy, there are multiple practical advantages to
463 applying DAMO as part of anaerobic effluent treatment processes.^{130, 131} With CH₄ as the sole
464 electron donor for DAMO microorganisms, no additional organic carbon sources would be
465 needed. Further, the slow growth rates of DAMO microorganisms such as *M. oxyfera* (doubling
466 time of 1–2 weeks), and low yields of DAMO microorganisms in general,^{122, 128} alleviate the
467 necessity of sludge disposal. Oxygen delivery via hollow fiber membrane units^{123, 127} or granular-
468 based optimization of oxygen levels¹²⁸ require further investigation to practically alleviate the
469 negative impacts of aeration on anammox/DAMO. Nonetheless, research thus far on MBfRs and
470 granular sludge reactors suggests that they may soon be a feasible basis for post-treatment of
471 anaerobic effluents.

472 3.4.3. MFCs as an alternative biological process

473 Microbial fuel cells (MFCs) have also been considered for effluent dissolved CH₄
474 management.¹³²⁻¹³⁵ MFCs are bioelectrochemical systems where exoelectrogenic
475 microorganisms oxidize organics and directly deposit electrons onto an anode.¹³⁶⁻¹³⁸ Methane,
476 as an organic substrate, can be used as an energy source to drive MFCs, converting it directly to
477 electricity.^{132-134, 139-141} For example, a study by McAnulty et al.¹³³ manipulated engineered
478 archaeal strains to produce acetate from CH₄ anaerobically via methyl coenzyme M reductase,
479 subsequently generating electricity in a two-chamber MFC. Chen et al.¹³⁴ also reported

480 electricity generation from CH₄ using a single-chamber MFC while observing microbial
481 interactions between aerobic methanotrophs and exoelectrogenic *Geobacter*. It should be
482 noted that these emerging biological processes, and specifically MFCs, require further
483 optimization in terms of capital cost reduction and achieving consistent treatment performance
484 before scaling up to pilot- and full-scale application.^{142, 143}

485 3.5. Implications of physical vs. biological systems for CH₄ mitigation

486 It should be noted that the aforementioned biological approaches, while potentially requiring
487 less energy input than membrane contactors and still mitigating GHG emissions, do not serve to
488 capture CH₄ for energy recovery. Although this is a significant limitation for DHS systems,
489 DAMO's use of CH₄ as an electron donor for nitrate reduction provides an alternative route to its
490 utilization in applications where nitrogen removal is a necessity (non-reuse effluent discharge).
491 On the other hand, the direct microbially-mediated energy potential of MFCs could provide a
492 particular advantage over both physical CH₄ recovery (using membrane contactors) and the
493 other biological approaches.

494 4. Future GHG management perspectives

495 4.1. N₂O as an energy recovery oxidant

496 N₂O, as a powerful oxidant, has the potential to be selectively produced in wastewater
497 treatment processes (e.g., via coupled aerobic-anoxic side-stream nitrogen removal) and serve
498 as a combustion oxidant in combination with CH₄.^{144, 145} In conventional WWTPs, N₂O off-gas
499 collection could be accomplished via the installation of covers on treatment unit processes,
500 however this may be impractical for nitrification due to the large volume of gas produced by
501 aeration. Although selective reduction of N₂O has been practiced industrially, similar processes
502 may not be cost-effective in large application to low N₂O containing gases as they require

503 catalysts and high reaction temperatures.¹⁴⁶ Nevertheless, with consistent N₂O production and
504 improved collection efficiency in newly designed processes,⁷⁸ this could be a worthwhile future
505 research topic.

506 4.2. Technologies for targeting CO₂ capture

507 Given the potential significance of non-biogenic CO₂ sources in municipal wastewater influents,
508 it is important to also consider possible means for direct CO₂ sequestration or capture. However,
509 considering the relatively high solubility of CO₂ in water and its potential cost of recovery, the
510 treatment of dissolved CO₂ in-situ using emerging technologies has recently become a topic of
511 interest. For example, phototrophic technologies relying on algae and/or phototrophic bacteria
512 could promote carbon fixation while simultaneously achieving nutrient removal.¹⁴⁷ Alternatively,
513 carbonic anhydrase, a ubiquitous enzyme capable of catalyzing the hydration of CO₂ into
514 bicarbonate and hydrogen at high rates, could potentially be incorporated into engineered
515 systems to sequester carbon directly.¹⁴⁷ Microbially assisted electrolytic systems also have the
516 potential to sequester and convert CO₂ to bicarbonate using either wastewater or seawater as
517 the electrolyte while producing beneficial products such as H₂.^{147, 148}

518 4.3. Methanotroph-based recovery of high-value end products

519 Methanotrophs can be metabolically engineered to synthesize a range of high-value products
520 including single cell proteins, biopolymers (e.g., polyhydroxyalkanoates, PHB), soluble
521 metabolites (e.g., methanol, formaldehyde, formate), lipids, lycopene, C30 carotenoid, lactic
522 acid and exopolysaccharides.¹⁴⁹⁻¹⁵² Methane oxidation is a multi-step process in which CH₄ is
523 oxidized to methanol, formaldehyde, formate, and CO₂ sequentially. Given that methanol
524 dehydrogenase is located in the periplasmic membrane of methanotrophs, methanol must be
525 transported out of the cell membrane in order for subsequent processes to ensue. Based on

526 this, methanotrophs can be genetically engineered or supplemented with inhibitors to suppress
527 this dehydrogenase and stop CH₄ oxidation at methanol,¹⁵³ which can then be collected and
528 enriched for use in MFCs (currently commercially available and used as portable electricity
529 sources). The application of these processes, among others, could be especially useful when
530 remote electricity generation is needed, the energy for which could be supplied exclusively from
531 treated wastewater.

532 4.4. Methane adsorbent-related technology

533 Recent studies have demonstrated that structures with high adsorption capacity and packing
534 density can be used to adsorb and store CH₄. For example, an investigation by Bagheri et al.¹⁵⁴
535 demonstrated that microporous activated carbon generated from corn cobs was capable of high
536 levels of CH₄ adsorption (150 v/v). Other materials such as constructed multilayer graphene
537 nanostructures (MGNs) with optimized layer distances were able to satisfy the U.S. department
538 of engineering target for adsorbents (180 v/v).¹⁵⁵ Although the aforementioned materials
539 require pressures of >100 psi to effectively sorb CH₄ into their structures (reducing their viability
540 from an energy and GHG footprint perspective), the recent synthesis of a monolithic metal-
541 organic framework has proven capable of reaching a CH₄ packing density of 259 v/v at pressures
542 previously comparable to those of half of its capacity.¹⁵⁶ The continuous improvement of
543 adsorptive materials and the potential for their exploration at lower sorption pressures could
544 lead to viable use for CH₄ capture, purification, and transport from wastewater effluents.

545 5. Perspectives on the direct comparison of CAS- and anaerobic-
546 based GHG emissions

547 Based on a normalized analysis of existing literature, herein we provide a parallel assessment of
548 CAS-based and anaerobic-based mainstream wastewater treatment using their dominant GHG
549 sources and assuming equivalent levels of treatment for effluents (i.e., nitrogen and COD
550 removal). Recent studies have shown that approximately 0.298 kg CO_{2e}/m³ of GHG emissions
551 come from electricity usage in conventional WWTPs (based on 0.472 kg CO₂/kWh energy carbon
552 footprint),^{17, 18, 34} with 50% of that energy demand being consumed by aeration.⁷ It is estimated
553 that roughly 25% of plant electricity use can be offset by energy produced from sludge
554 digestion.⁷ Taking these values into account, total fossil fuel-generated emissions from
555 conventional treatment would be on the order of 0.224 kg CO_{2e}/m³ DWW. Total fugitive CH₄
556 emissions were also included at an average of 0.095 kg CO_{2e}/m³.⁴⁵

557 Assuming full-scale mainstream anaerobic treatment energy demands are comparable to those
558 of conventional WWTPs before considering aeration requirements, it can be anticipated that
559 their electricity consumption accounts for approximately 0.149 kg CO_{2e}/m³ DWW. The amount
560 of energy achievable from direct biogas recovery (headspace) was further calculated based on
561 methane loss values extracted from Figure 3 at 25°C and 10°C (15 and 50 mg CH₄/L,
562 respectively). Assuming a 95% conversion of incoming COD (430 mg/L) to CH₄, energy density of
563 55.5 MJ/kg, conversion efficiency to electricity of 35%, and a CO₂ emission factor from electricity
564 usage of 0.472 kg CO₂/kWh,¹⁵⁷ it is estimated that anaerobic mainstream treatment electricity-
565 associated GHG footprints could be reduced to below 0.02 kg CO_{2e}/m³ at 10°C, while actually
566 achieving energy positive operation at 25°C (-0.073 kg CO_{2e}/m³). Based on these calculations, it
567 can be concluded that mainstream anaerobic treatment has the potential to more significantly

568 offset electricity-associated GHG emissions when compared to conventional WWTPs with
569 anaerobic digestion (0.224 kg CO_{2e}/m³). However, without downstream CH₄ recovery, anaerobic
570 effluents would contribute GHG emissions of approximately 0.51 and 1.70 kg CO_{2e}/m³ at 25°C
571 and 10°C, respectively (using CH₄ GWP of 34 and dissolved methane-temperature relationship
572 obtained from Figure 3).

573 N₂O emissions from the nitrogen removal process in WWTPs have been identified as the most
574 widely varying and least predictable of GHG sources (ranging from 0 to 14.6% of incoming
575 nitrogen). Nonetheless, an analysis of several representative full-scale studies of conventional
576 anoxic-oxic processes revealed an average emission factor of 1.5%,^{31, 32, 36, 158-160} resulting in N₂O
577 emissions of 0.281 kg CO_{2e}/m³ DWW for conventional WWTPs (assuming influent of 20 mg N/L
578 and N₂O GWP of 298). If nitrification coupled with anammox is employed as the nitrogen removal
579 process for mainstream anaerobic treatment and an average nitrogen to N₂O ratio of 2.8% is
580 used (estimated from full-scale nitrification-anammox studies),^{70, 71, 161, 162} N₂O emissions for
581 anaerobic treatment can be calculated as 0.529 kg CO_{2e}/m³ WW. The relatively higher emissions
582 observed for nitrification-anammox have been attributed to a lack of process optimization for N₂O
583 mitigation,¹⁰ which can likely be improved upon significantly in future research.

584 Therefore, total GHG emissions from CAS WWTPs are significantly lower than mainstream
585 anaerobic systems, even at 25°C (0.599 vs. 0.966 kg CO_{2e}/m³ WW). Anaerobic treatment GHG
586 footprints would likely be exacerbated at lower ambient temperatures, reaching up to 2.25
587 CO_{2e}/m³ at 10°C, if no effluent recovery was employed. As outlined in this review, however,
588 emerging techniques for both nitrogen and dissolved CH₄ removal/recovery could effectively
589 negate these outstanding issues. If, for example, energy-efficient dissolved CH₄ recovery is
590 employed and comparable N₂O emissions are achieved through nitrogen removal processes
591 optimization, mainstream anaerobic system GHG footprints would easily drop below those

592 calculated for current CAS WWTP processes. Further, recent research has implicated
593 mainstream anaerobic effluents as likely to become acceptable for direct irrigation reuse from a
594 microbial safety perspective.^{163, 164} This application of nutrient-rich treated effluents could
595 negate the necessity of nitrogen removal, essentially allowing for the elimination of direct N₂O
596 emissions from mainstream anaerobic treatment and such systems approaching carbon
597 neutrality.

598 6. Conclusions

599 Existing literature on WWTP GHGs has reported broadly varying total emissions ranging from
600 0.243 to 2.4 kg CO_{2e}/m³ WW. A unified and comprehensive plant-wide approach inclusive of all
601 direct and indirect emissions is necessary for accurate WWTP carbon footprint interpretation.
602 Overall, the most significant obstacle facing GHG mitigation in CAS WWTPs is associated with
603 understanding N₂O generation, whereas for the sustainability of mainstream anaerobic
604 wastewater treatment, dissolved CH₄ emissions are of greatest concern. Other specific
605 observations of this review are summarized as follows:

- 606 • N₂O emissions are both dominant and highly variable in conventional aerobic-based
607 WWTPs (0 to 95% of N for lab-scale and 0 to 14.6% of N for full-scale), with several
608 critical factors influencing this variability including: DO, pH, nitrite, carbon source
609 availability and ammonium loading.
- 610 • More research is specifically needed in elucidating the pathways involved in N₂O
611 formation (i.e., nitrifier denitrification, heterotrophic denitrification, and hydroxylamine
612 oxidation) at different operational conditions, which can be then used to correlate
613 practical mitigation strategies with specific processes and configurations.

- 614 • Dissolved CH₄ contributions in mainstream anaerobic treatment account for the
615 majority of GHG emissions. Anaerobic system GHG emissions are inversely correlated
616 with operational temperature due to increasing CH₄ solubility and supersaturation
617 (Section 4.1).
- 618 • Analysis of membrane contactors for physical dissolved CH₄ removal showed that for
619 sweep gas systems, gas to liquid (G/L) ratio is a critical parameter influencing CH₄
620 removal efficiency and off-gas CH₄ concentration. Vacuum driven membrane contactors,
621 although capable of high-quality gas recovery, require operation at TMPs below 50 kPa
622 to achieve energy neutrality.
- 623 • Several emerging methods for dissolved CH₄ recovery are likely to play significant roles
624 in future management of dissolved CH₄. For example, DAMO combined with anammox
625 could allow for the simultaneous removal of both nitrogen and CH₄ from anaerobic
626 effluents.

627 To significantly reduce WWTP GHG emissions, future research on CAS must focus on N₂O
628 management strategies to minimize emissions. For anaerobic systems, both efficient CH₄ and
629 nitrogen resource recovery must be achieved without introducing incidental increases in N₂O
630 generation. The accomplishment of this goal appears to be within reach, given the prospects of
631 emerging CH₄ recovery processes and likelihood of effluent reuse.

632 Acknowledgements:

633 Siming Chen is partially funded by the China Scholarship Council. Moustapha Harb is partially
634 funded by Water for Agriculture grant no. 2016-68007-25044 from the USDA National Institute
635 of Food and Agriculture. The research was supported by the University of Southern California.

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