

**This item is the archived peer-reviewed author-version of:**

Nitrous oxide emissions and carbon footprint of decentralized urine fertilizer production by nitrification and distillation

**Reference:**

Faust Valentin, Gruber Wenzel, Ganigue Ramon, Vlaeminck Siegfried, Udert Kai M..- Nitrous oxide emissions and carbon footprint of decentralized urine fertilizer production by nitrification and distillation  
ACS ES&T engineering - ISSN 2690-0645 - 2:9(2022), p. 1745-1755  
Full text (Publisher's DOI): <https://doi.org/10.1021/ACSESTENGG.2C00082>  
To cite this reference: <https://hdl.handle.net/10067/1895990151162165141>

# Nitrous oxide emissions and carbon footprint of decentralized urine fertilizer production by nitrification and distillation

Valentin Faust<sup>a,b</sup>, Wenzel Gruber<sup>a,b</sup>, Ramon Ganigué<sup>c,d</sup>, Siegfried E. Vlaeminck<sup>d,e</sup>, Kai M. Udert<sup>a,b\*</sup>

1 <sup>a</sup> Eawag, Swiss Federal Institute of Aquatic Science and Technology, 8600 Dübendorf, Switzerland

2 <sup>b</sup> ETH Zürich, Institute of Environmental Engineering, 8093 Zürich, Switzerland

3 <sup>c</sup> Center for Microbial Ecology and Technology (CMET), Faculty of Bioscience Engineering, Ghent University, 9000 Gent,  
4 Belgium

5 <sup>d</sup> Centre for Advanced Process Technology for Urban Resource recovery (CAPTURE), Frieda Saeysstraat 1, 9052 Gent,  
6 Belgium

7 <sup>e</sup> Research Group of Sustainable Energy, Air and Water Technology, Department of Bioscience Engineering, Faculty of  
8 Science, University of Antwerp, 2020 Antwerpen, Belgium

9

10 Emails of the authors: [Valentin.Faust@eawag.ch](mailto:Valentin.Faust@eawag.ch), [Wenzel.Gruber@eawag.ch](mailto:Wenzel.Gruber@eawag.ch), [Ramon.Ganigue@UGent.be](mailto:Ramon.Ganigue@UGent.be),

11 [Siegfried.Vlaeminck@uantwerpen.be](mailto:Siegfried.Vlaeminck@uantwerpen.be), [Kai.Udert@eawag.ch](mailto:Kai.Udert@eawag.ch)

12 \* Corresponding author: [Kai.Udert@eawag.ch](mailto:Kai.Udert@eawag.ch)

13

14

15 Published in ACS ES&T Engineering:

16 <https://doi.org/10.1021/acsestengg.2c00082>

17 -

18

19 **Abstract**

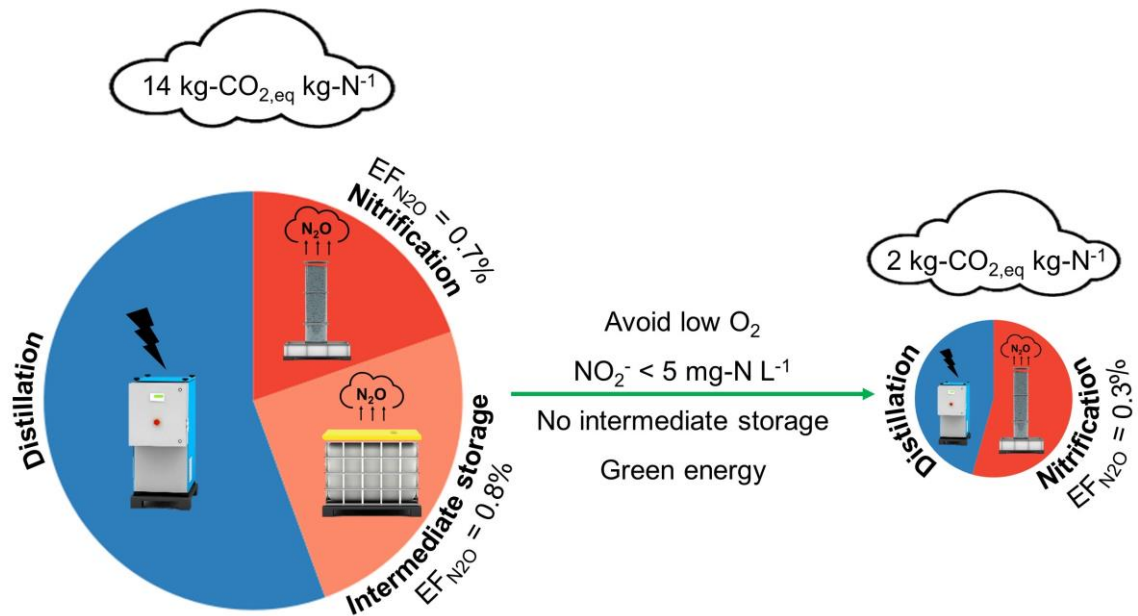
20 Combining partial nitrification, granular activated carbon (GAC) filtration, and distillation is a well-studied  
21 approach to convert urine into a fertilizer. To evaluate the environmental sustainability of a technology, the  
22 operational carbon footprint and therefore nitrous oxide (N<sub>2</sub>O) emissions should be known, but N<sub>2</sub>O emissions  
23 from urine nitrification have not been assessed yet. Therefore, N<sub>2</sub>O emissions of a decentralized urine nitrification  
24 reactor were monitored for one month. During nitrification, 0.4% to 1.2% of the total nitrogen load was emitted  
25 as N<sub>2</sub>O-N with an average N<sub>2</sub>O emission factor (EF<sub>N<sub>2</sub>O</sub>) of 0.7%. Additional N<sub>2</sub>O was produced during anoxic  
26 storage between nitrification and GAC filtration with an estimated EF<sub>N<sub>2</sub>O</sub> of 0.8%, resulting in an EF<sub>N<sub>2</sub>O</sub> of 1.5%  
27 for the treatment chain. N<sub>2</sub>O emissions during nitrification can be mitigated by 60% through avoiding low  
28 dissolved oxygen or anoxic conditions and nitrite concentrations above 5 mg-N L<sup>-1</sup>. Minimizing the hydraulic  
29 retention time between nitrification and GAC filtration can reduce N<sub>2</sub>O formation during intermediate storage by  
30 100%. Overall, the N<sub>2</sub>O emissions accounted for 45% of the operational carbon footprint of 14 kg-CO<sub>2,eq</sub> kg-N<sup>-1</sup>  
31 for the urine fertilizer production. Using electricity from renewable sources and applying the proposed N<sub>2</sub>O  
32 mitigation strategies could potentially lower the carbon footprint by 85%.

33 **Keywords**

34 Greenhouse gas emissions; Resource recovery; MELiSSA; Nitrite sensor; Digester supernatant

35

36 **Graphical abstract**



37

## 38           **1 Introduction**

39    In developed countries, urine is conventionally mixed with other liquid household waste streams and  
40    transported to a centralized wastewater treatment plant (WWTPs), where most of the nitrogen is  
41    removed by nitrification and denitrification and released into the atmosphere as  $N_2$ .<sup>1</sup> Simultaneously,  
42    atmospheric  $N_2$  is converted in the chemical Haber-Bosch process to  $NH_3$  that can be further processed  
43    into several nitrogen-based fertilizers, such as urea or ammonium nitrate.<sup>2</sup> An alternative approach is to  
44    separate urine at the source and directly produce a fertilizer that can partly substitute synthetic fertilizers  
45    and reduces the nitrogen and phosphorus loads to WWTP.<sup>3</sup> This direct recovery and local shortcut of  
46    the nitrogen cycle can potentially reduce nutrient emissions to the environment,<sup>4-5</sup> which is important as  
47    the global nitrogen and phosphorus cycles have exceeded their safe planetary boundaries.<sup>6</sup> In addition,  
48    urine source separation is the primary approach in regenerative life support systems for space application  
49    such as the Micro-Ecological Life Support System Alternative (MELiSSA).<sup>7-8</sup>

50    One well-studied treatment chain to convert urine into a liquid ammonium nitrate fertilizer is through  
51    partial nitrification, granular activated carbon (GAC) filtration and distillation. In the system, urea is  
52    hydrolyzed to ammonia and then partially oxidized to nitrate<sup>9</sup>. In the GAC, micropollutants are  
53    removed<sup>10</sup>, and in the distiller, pathogens are killed and the volume is reduced to produce the fertilizer  
54    product<sup>9</sup>. In 2018, this urine fertilizer has been approved by the Swiss Federal Office for Agriculture for  
55    the fertilization of edible crops ([www.vunanexus.com/aurin-fertiliser](http://www.vunanexus.com/aurin-fertiliser)). To evaluate the environmental  
56    sustainability of a technology, life cycle assessments (LCA) on impact categories such as global  
57    warming potential, eutrophication potential and acidification potential are required.<sup>11</sup> As a first step,  
58    estimating the operational carbon footprint allows a simple comparison between different scenarios,  
59    with the system boundaries starting at collected urine and ending at a comparable fertilizer.

60    Daelman et al.<sup>12</sup> showed that direct nitrous oxide ( $N_2O$ ) emissions can be the largest contributor to the  
61    carbon footprint of wastewater treatment, accounting for up to 80% of the operational carbon footprint  
62    of a WWTP.  $N_2O$  from wastewater treatment is mainly produced by ammonia-oxidizing bacteria (AOB)  
63    through hydroxylamine oxidation and nitrifier denitrification,<sup>13</sup> and by heterotrophic denitrifying  
64    bacteria.<sup>14</sup>  $N_2O$  emissions measured at WWTP are highly dynamic and depend strongly on factors such

65 as influent characteristics, nitrogen removal efficiency, and stability of nitrification.<sup>15</sup> N<sub>2</sub>O emissions  
66 are usually reported as emission factors (EF<sub>N<sub>2</sub>O</sub>) relative to the total nitrogen (TN) load in the influent  
67 expressed as [g N<sub>2</sub>O-N g N<sup>-1</sup>] or [%]. For mainstream nitrification in WWTPs, EF<sub>N<sub>2</sub>O</sub> generally range  
68 from 0.01 to 2% of the TN load for the majority of the different process groups.<sup>16</sup> For full-scale  
69 continuous long-term studies, an average EF of 0.9% has recently been suggested for WWTP with  
70 nitrification and denitrification,<sup>15</sup> which is lower than the EF<sub>N<sub>2</sub>O</sub> of 1.6% recommended by the updated  
71 IPCC guidelines as an assumption for WWTP.<sup>17</sup> The EF<sub>N<sub>2</sub>O</sub> from sidestream processes are generally  
72 considered to be higher ranging from 0.2 to 5.1%, which is among others related to higher ammonia  
73 oxidation rate and nitrite accumulation.<sup>16</sup>

74 To our knowledge, N<sub>2</sub>O emissions from urine nitrification have not been studied before.  
75 Martin<sup>18</sup> assumed an EF<sub>N<sub>2</sub>O</sub> of 0.5% for the LCA of urine nitrification, but no N<sub>2</sub>O measurements were  
76 made. Other LCAs of urine recovery systems focused on treatment technologies such as reverse  
77 osmosis,<sup>19</sup> struvite precipitation,<sup>19-20</sup> ion exchange,<sup>19, 21</sup> and microbial electrolysis,<sup>20</sup> which all were  
78 assumed to emit no N<sub>2</sub>O. Only in the case of extended urine storage for hygienization, Spangberg et al.<sup>22</sup>  
79 estimated N<sub>2</sub>O emissions of 1% of ammonia nitrogen emitted to the air during collection and storage.

80 Partial urine nitrification has been reported to have high ammonium oxidation rates up to  
81 640 mg-N L<sup>-1</sup> d<sup>-1</sup>, high nitrite concentrations (1 to 20 mg-N L<sup>-1</sup>) compared to mainstream nitrification  
82 and a low chemical oxidation demand (COD) to nitrogen ratio in the influent of about 1 g-COD g-N<sup>-1</sup>.<sup>9</sup>  
83 These are all factors that potentially promote N<sub>2</sub>O production.<sup>23</sup> However, influent concentrations and  
84 operational temperatures are relatively constant because there is no mixing with storm water and no  
85 temperature related seasonality due to the in-building settings. These two factors are potentially leading  
86 to lower N<sub>2</sub>O emissions.<sup>15, 24-25</sup> Since it is difficult to extrapolate N<sub>2</sub>O emissions for urine nitrification  
87 based on reports of municipal wastewater or digester supernatant treatment, in this study, the N<sub>2</sub>O  
88 emissions and the carbon footprint of a decentralized urine fertilizer production setup consisting of a  
89 nitrification, GAC filtration and distillation were determined. The study had the following three research  
90 objectives:

- 91       • Quantify the N<sub>2</sub>O emissions of urine fertilizer production by partial nitrification, GAC filtration  
92       and distillation.
- 93       • Determine the influencing factors enhancing N<sub>2</sub>O production and emission, and propose  
94       mitigation strategies.
- 95       • Determine the contribution of N<sub>2</sub>O emissions to the operational carbon footprint of urine  
96       fertilizer production.

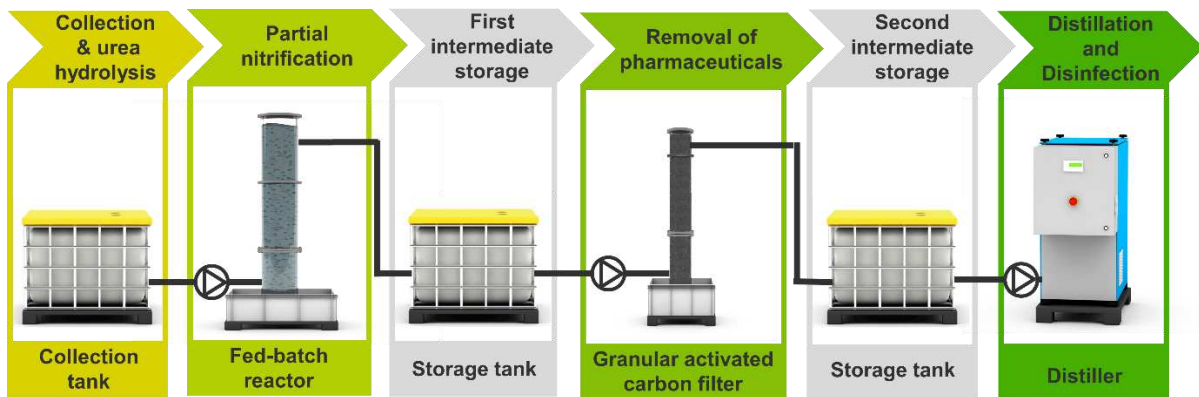
## 97        2    **Materials and methods**

### 98        2.1    **Urine fertilizer production system**

99        The investigated treatment system collected urine from more than 100 employees and was located at the  
100        Swiss Federal Institute of Aquatic Science and Technology (Eawag, Dübendorf, Switzerland). The  
101        decentralized treatment system consisted of four steps (**Figure 1**). First, urea was hydrolyzed to free  
102        ammonia ( $\text{NH}_3$ ) and ammonium ( $\text{NH}_4^+$ ) under anaerobic conditions as described in Udert et al.<sup>26</sup> in two  
103        1000-L collection tanks with a hydraulic retention time (HRT) of around 26 days (average, data analysis  
104        2018 to 2021, **SI 1**). Subsequently, ammonia was partially oxidized to nitrate in two 120-L nitrification  
105        reactors. The nitrification reactors were operated in fed-batch mode with suspended activated sludge.  
106        One fed-batch cycle consisted of an aeration phase during which 12 L were fed to the reactor, a settling  
107        phase of typically 30 minutes without aeration, and a decant phase of 2 minutes during which 10% of  
108        the reactor volume was extracted. No base is added in the partial nitrification process. Instead, the pH is  
109        controlled with the urine inflow via a narrow two-position controller. Once the pH reaches the lower  
110        setpoint due to protons released during nitrification, the inflow is turned on, causing the pH to increase  
111        due to the higher pH and alkalinity in the urine inflow. A faster nitrification rate therefore resulted in  
112        higher flow rates. The available alkalinity in urine ( $\sim 1$  mole-Alkalinity mole- $\text{N}^{-1}$ ) is responsible that  
113        only about 50% of the total ammoniacal nitrogen ( $\text{TAN} = \text{NH}_3\text{-N} + \text{NH}_4^+\text{-N}$ ) is converted to nitrate  
114        nitrogen ( $\text{NO}_3^-\text{-N}$ ), as each nitrified mole of N produces two moles of  $\text{H}^+$ . Despite only converting  
115        around half of the TAN, ammonia volatilization is prevented because nitrification causes a pH drop so  
116        that free ammonia converts virtually fully to non-volatile ammonium. Typically, the pH in the reactor  
117        is between 5.8 and 6.7 (5<sup>th</sup> and 95<sup>th</sup> percentile, data analysis 2018 to 2021, **SI 1**). Higher pH setpoints  
118        can accelerate the nitrification process but can also lead to nitrite accumulation and even partial  
119        nitritation.<sup>9</sup> Therefore, the nitrite concentration has to be monitored frequently. After nitrification, the  
120        urine was stored in a 500-L intermediate storage tank with a working volume of 200 to 215 L. Once the  
121        higher volume level was reached, 15 to 25 L of urine were pumped through the granular activated carbon  
122        (GAC) filter, where pharmaceuticals are removed as described by Köpping et al..<sup>10</sup> The effluent was



123 stored in 500-L intermediate storage tank with a working volume of 50 to 400 L. Once the higher volume  
 124 level was reached, 350 L of urine was pumped to a vapor compression vacuum distiller, where pathogens  
 125 are killed and the nutrients were concentrated by a factor of 10 to 15 as described by Fumasoli, et al. <sup>27</sup>.  
 126 Because the GAC and the distiller were dimensioned for higher flow rates than the maximum observed  
 127 flow rate of the nitrification, the HRT in the intermediate storage depends on the nitrification rate. The  
 128 final product of the urine treatment was a liquid ammonium nitrate fertilizer with a nitrogen content  
 129 (w/w) of roughly 4% ([www.vunanexus.com/aurin-fertiliser](http://www.vunanexus.com/aurin-fertiliser)). If more urine was collected than the  
 130 treatment capacity of the urine fertilizer production, the excess urine had to be flushed to the wastewater  
 131 treatment plant.



**Figure 1:** Decentralized urine fertilizer production system consisting of urea hydrolysis, partial nitrification, pharmaceutical removal and distillation.

## 132 2.2 N<sub>2</sub>O emissions from the nitrification process

133 The N<sub>2</sub>O concentration in the off-gas of one 120-L urine nitrification reactor was measured continuously  
 134 for one month (5 August 2020 to 7 September 2020) with a resolution of ten seconds. For the  
 135 measurement, 1 L min<sup>-1</sup> was diverted from the off-gas, dehumidified by cooling, and measured at a  
 136 controlled and constant temperature of 60°C with a nondispersive infrared sensor (NDIR, X-stream  
 137 X2GP, Emerson). The airflow (Q<sub>air</sub>) in the nitrification reactor was controlled with a series of mass flow  
 138 controllers (red-y smart controller GSC, Vögtlin Instruments GmbH). The EF<sub>N<sub>2</sub>O</sub> [%] was calculated  
 139 according to **Equation 1**,

140 
$$EF_{N_2O} = \frac{Q_{air} * C_{N_2O-N,off-gas}}{Q_{influent} * C_{TN,influent}} * 100\% \quad (1)$$

141 where  $Q_{air}$  is the airflow supplied to the nitrification reactor [ $L \text{ min}^{-1}$ ],  $C_{N_2O-N,off-gas}$  is the  $N_2O$   
142 concentration in the off-gas of the nitrification reactor [ $mg-N \text{ L}^{-1}$ ],  $Q_{influent}$  is the pump rate to the  
143 nitrification reactor [ $L \text{ min}^{-1}$ ], and  $C_{TN,influent}$  the TN concentration in the influent [ $mg-N \text{ L}^{-1}$ ].  $C_{TN,influent}$   
144 was estimated based on the TAN measurement in the collection tanks, assuming that the TAN accounts  
145 for 90% of the TN in stored urine.<sup>28</sup> In addition, nitric oxide (NO) was measured in a range of 0 ppm to  
146 150 ppm during the first half of the measurement campaign using the same NDIR unit as for  $N_2O$ . While  
147 NO is not used for the carbon footprint, it can provide information on potential  $N_2O$  formation pathways  
148 because it is an intermediate in heterotrophic and nitrifier denitrification.<sup>23</sup>

149 Usually,  $N_2O$  measurement campaigns should extend over the seasonal variations of at least one year.<sup>29</sup>  
150 However, in the investigated system no strong seasonal temperature change patterns (seasonal  
151 temperature boxplot, **SI 1**) or wet-weather related influent fluctuations occur due to the separate in-  
152 house collection of urine. In partial urine nitrification, changes of environmental conditions are primarily  
153 induced by the operators. Therefore, the influence of operator-induced environmental conditions was  
154 evaluated by testing a range of typical pH setpoints, airflow rates and settling times during the  
155 measurement campaign. To determine typical operation conditions for partial urine nitrification,  
156 nitrification data from 2018 to 2021 were evaluated (boxplot of operational conditions, **SI 1**). During  
157 the measurement campaign, pH was increased stepwise from 5.75 to 6.45 before decreasing it again.  
158 The airflow rate was adjusted to obtain dissolved oxygen (DO) concentrations in the range of 0.5 to  
159  $5 \text{ mg L}^{-1}$  during the aerated phase. Changing the pH setpoints and the airflow further allowed influencing  
160 the nitrite concentration in the reactor, as high pH values and low DO concentrations can trigger nitrite  
161 accumulation.<sup>9</sup> In this way, nitrite peaks up to  $20 \text{ mg-N L}^{-1}$  were targeted in the second half the  
162 measurement campaign. In addition to the settling time of 30 minutes, two shorter phases of 6 and 15  
163 minutes were tested to determine the influence of the settling time.

164

165

### 2.3 N<sub>2</sub>O emissions from intermediate storage, GAC filtration and distillation

166

167 To estimate N<sub>2</sub>O production in the two intermediate storage tanks, liquid N<sub>2</sub>O samples were taken  
168 weekly for three weeks (8 January 2021 to 29 January 2021). Because stratification might have occurred  
169 in the tanks, samples were taken at the same height at which the urine was pumped to the next stage  
170 (20 cm above the bottom). The concentrations in the samples therefore represented the effluent  
171 concentrations. Samples were also taken simultaneously from both intermediate tanks and the influent  
172 and effluent of the GAC filter on a one-time basis on 31 March 2021. No samples were taken from the  
173 collection tank because no N<sub>2</sub>O production was expected due to inhibition of nitrification by the high  
174 concentration of free ammonia.

175 Dissolved N<sub>2</sub>O concentrations were determined with headspace gas chromatography as in Woszczyk  
176 and Schubert<sup>30</sup>. For this purpose, samples were filled in 120-mL serum bottles, and the pH was increased  
177 to pH > 11 with sodium hydroxide to inhibit microbial activity. Back in the laboratory, 30 mL sample  
178 aliquots were displaced by adding N<sub>2</sub> gas to create a headspace. The N<sub>2</sub>O concentration in the headspace  
179 was measured with a GC column (GS Carbonplot 30m x 0.32mm x 3µm, Ref. 113-3133, Agilent  
180 Technologies modified by Jasco) with electron capture detection. The measurement device was  
181 calibrated with reference gas mixtures from Carbagas for a range of 0.1 to 30 ppm, and the samples were  
182 diluted accordingly with N<sub>2</sub> to fit within this range. The dissolved N<sub>2</sub>O concentration was determined  
183 using the solubility coefficients of Weiss and Price<sup>31</sup> (see equations in SI 2). The measurement  
184 uncertainty (standard deviation) for the determination of the dissolved N<sub>2</sub>O concentration was 15%.

185 In addition, storage experiments were performed to investigate the influence of storage duration and  
186 nitrite concentration on N<sub>2</sub>O production from partially nitrified urine. The aim was to determine whether  
187 and how N<sub>2</sub>O production changes over time during storage. Nitrite was added because the nitrite  
188 concentrations in the nitrification effluent can vary between 0.1 to 20 mg-N L<sup>-1</sup> and can strongly  
189 influence N<sub>2</sub>O production<sup>32</sup>. Therefore, 14 laboratory bottles (500 mL) were filled with effluent from  
190 the nitrification reactor with equal ammonium and nitrate concentrations of about 1300 mg-N L<sup>-1</sup> and  
191 nitrite concentrations of about 0.1 mg-N L<sup>-1</sup>. Nitrite was spiked to half of them to obtain final  
192 concentrations of about 10 mg-N L<sup>-1</sup>. One bottle with and one without additional nitrite were harvested

193 every three to four days for three weeks and prepared for headspace gas chromatography. Last but not  
194 least, one bottle (500 mL) was filled with effluent from the GAC filter and harvested after one week for  
195 headspace gas chromatography. For the distillation, it was assumed, that no N<sub>2</sub>O would be produced or  
196 consumed, because the operating temperature of 80°C should be too high for biological N<sub>2</sub>O production  
197 or consumption and too low for abiotic N<sub>2</sub>O processes such as thermal decomposition.<sup>33</sup> Instead, all  
198 dissolved N<sub>2</sub>O is expected to be stripped during distillation process at the latest. Therefore, the EF was  
199 derived from the dissolved N<sub>2</sub>O concentration according to **Equation 2**,

$$200 \quad EF_{N_2O} = \frac{C_{N_2O-N}}{C_{TN}} * 100\% \quad (2)$$

201 where C<sub>N<sub>2</sub>O-N</sub> is the concentration of dissolved N<sub>2</sub>O [mg-N L<sup>-1</sup>]. For the EF<sub>N<sub>2</sub>O</sub> during intermediate  
202 storage, TN concentration in the solution C<sub>TN</sub> was used [mg-N L<sup>-1</sup>] instead of the TN concentration in  
203 the influent because no influent measurement was available during this period. Nitrogen losses between  
204 the influent and the storage tanks should be small.<sup>34</sup> Here, TN was simplified as the sum of NH<sub>4</sub><sup>+</sup>-N,  
205 NO<sub>3</sub><sup>-</sup>-N, NO<sub>2</sub><sup>-</sup>-N, and N<sub>2</sub>O-N.

## 206 **2.4 Analytical methods**

207 Samples for the analyses of cations (ammonium, potassium, sodium, calcium and magnesium) and  
208 anions (nitrate, phosphate, sulfate and chloride) were filtered through a 0.45 μm GF/PET filter  
209 (Chromafil, Macherey-Nagel) and measured with ion chromatography (881 compact IC pro, Metrohm).  
210 Nitrite and dissolved COD were measured with spectrophotometric cuvette tests (LCK 341 resp.  
211 LCK114, Hach Lange GmbH) using a spectrophotometer from Hach Lange GmbH (DR 2800, Hach  
212 Lange GmbH). Total suspended solids and volatile suspend solids were measured according to APHA  
213 (2012) standard protocols. An optical oxygen sensor (Oxymax COS61D, Endress+Hauser) was used to  
214 measure DO, and pH (Orbisint CPS11D, Endress+Hauser) was measured continuously and calibrated  
215 weekly. An electrochemical sensor enabled online measurements of nitrite during the second half of the  
216 measurement campaign.<sup>35</sup> The sensor was calibrated *in situ* with offline nitrite measurements, and a new

217 calibration curve was generated every time the sensor was cleaned, which was at least every week (see  
218 **SI 3** for calibration curves).

## 219 **2.5 Operational carbon footprint calculation**

220 The direct N<sub>2</sub>O and methane (CH<sub>4</sub>) emissions, and the indirect carbon footprint of the electricity demand  
221 were considered for the operational carbon footprint of the urine fertilizer production. Direct carbon  
222 dioxide (CO<sub>2</sub>) emissions from the nitrification reactor were measured during the second half of the  
223 measurement campaign, but following the IPCC guidelines,<sup>36</sup> they were not taken into account for the  
224 footprint calculation because they are considered biogenic. Continuous CH<sub>4</sub> off-gas measurements  
225 during nitrification were conducted during two weeks with the same measurement setup as for N<sub>2</sub>O with  
226 a measurement range of 0 to 500 ppm. In addition, grab samples from the headspace of the collection  
227 tanks were analyzed by NDIR to determine if considerable amounts of CH<sub>4</sub> were released in the  
228 anaerobic collection tanks. For the air exchange of the collection tanks with the environment, it was  
229 assumed that the tanks are half full on average and that the entire headspace is exchanged once a day,  
230 resulting in an air leakage of 1000 L d<sup>-1</sup>. A global warming potential of 265 g-CO<sub>2,eq</sub> g-N<sub>2</sub>O<sup>-1</sup> and  
231 28 g-CO<sub>2,eq</sub> g-CH<sub>4</sub><sup>-1</sup> was applied according to the IPCC assessment report 5<sup>37</sup> for a 100-year period.

232 For the energy demand, the distiller, the aeration system, pumps and the process control were considered  
233 (**Table 1**). According to Fumasoli et al.<sup>27</sup>, the energy demand of the distiller, including pumping, was  
234 31 kWh kg-N<sup>-1</sup> when related to the total nitrogen in the influent of the nitrification. Since compressed  
235 air from a central facility was used for the aeration of the nitrification reactor, the energy demand could  
236 not be measured. Instead, the aeration from another urine fertilizer production system (three 300-L fed-  
237 batch reactors, UrinExpress, [www.vuna.ch/en/urin-recycling-technologie](http://www.vuna.ch/en/urin-recycling-technologie)) was used and scaled  
238 according to the average airflow rate and the reactor height. For consistency, the energy demand of the  
239 two remaining pumps and the process control system were also taken from the UrinExpress. More details  
240 can be found in the **SI 4**.

241 **Table 1:** Energy demand in [Wh L<sub>urine</sub><sup>-1</sup>] and [kWh kg-N<sup>-1</sup>] for the distiller, aeration, pumping and process  
242 control.

	[Wh L <sub>urine</sub> <sup>-1</sup> ]	[kWh kg-N <sup>-1</sup> ]	Source
Distiller	107	31	Fumasoli et al. <sup>27</sup>
Aeration	5.9	1.7	UrinExpress, own data
Pumping	3.2	0.9	UrinExpress, own data
Process control	3.2	0.9	UrinExpress, own data

243

244 A European electricity mix of 230 g-CO<sub>2,eq</sub> kWh<sup>-1</sup> was used for the measurement campaign.<sup>38</sup> To  
245 investigate the impact of a greener energy mix, a fictional renewable energy production scenario was  
246 used consisting of 50% onshore wind and 50% photovoltaic, resulting in a specific CO<sub>2</sub> emission of  
247 26 g-CO<sub>2,eq</sub> kWh<sup>-1</sup>.<sup>37</sup>

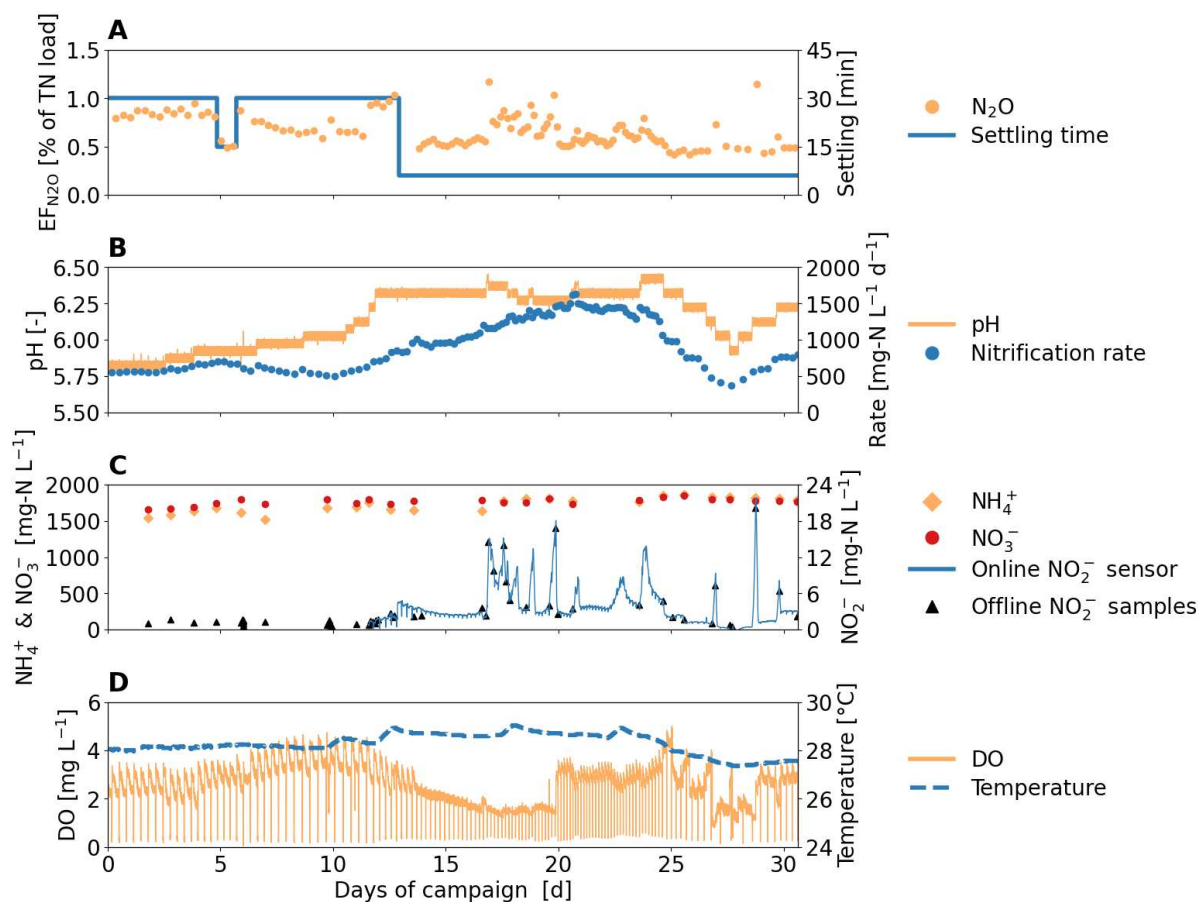
248 Monte Carlo simulations were performed to analyze the uncertainty of the carbon footprint. The standard  
249 deviations of the parameter values were estimated or calculated and 10'000 simulations were run to  
250 determine the standard deviation of the operational carbon footprint. For the N<sub>2</sub>O and the CH<sub>4</sub> from the  
251 nitrification, the standard deviation observed during the measurement campaign was used, and it was  
252 assumed that the uncertainty of the measurement device was negligible. For the N<sub>2</sub>O from the  
253 intermediate storage, the standard deviation of the storage durations observed during the main  
254 measurement campaign, and the measurement uncertainty of the headspace gas chromatography method  
255 were considered. For the CH<sub>4</sub> emissions from the collection tanks, the standard deviation of the  
256 measured concentration and an uncertainty for the air exchange rate was included. The standard  
257 deviation of the distiller was included according Fumasoli, et al. <sup>27</sup>, taking also into account the different  
258 TN concentrations during the measurement campaign. Since the aeration, pumping and process control  
259 had only a minor impact on the operational carbon footprint, a general standard deviation of 50% was  
260 considered for all of them.

261

262 **3 Results**

263 **3.1 N<sub>2</sub>O emissions during nitrification**

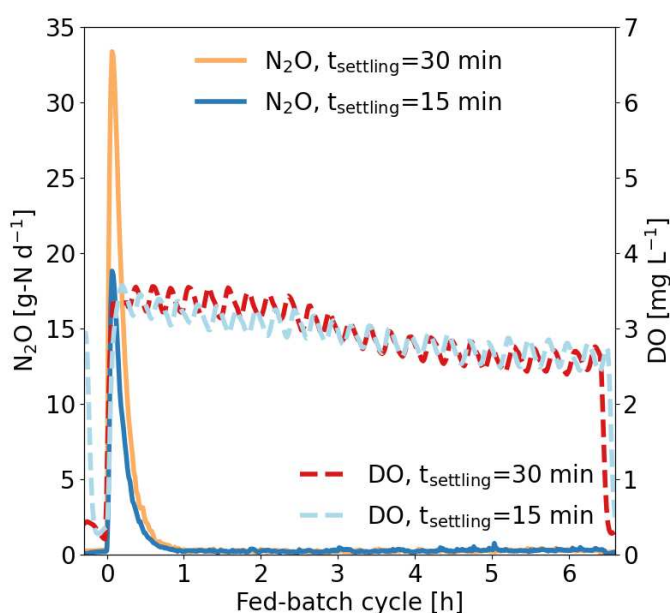
264 The average EF<sub>N<sub>2</sub>O</sub> for the nitrification over the whole measurement campaign was 0.7 ± 0.2% of the  
265 TN load. The EF<sub>N<sub>2</sub>O</sub> per fed-batch cycle varied between 0.4% and 1.2% of the TN load, and no diurnal  
266 patterns were found **Figure 2A**). Instead, the settling time had a strong influence on the EF<sub>N<sub>2</sub>O</sub>. A  
267 temporary reduction in settling time from 30 minutes to 15 minutes on day 5, while maintaining all other  
268 operational variables, led to a reduction in N<sub>2</sub>O emissions of 40%, which was reversible once the settling  
269 time was increased again. In the second half of the measurement campaign, the settling time was  
270 permanently reduced to 6 minutes based on the minimally required sludge settling duration (settling  
271 curve in **SI 5**), which again led to a decrease in N<sub>2</sub>O emissions.



272  
273 **Figure 2:** Performance and settings of the nitrification reactor during the measurement campaign. (A) N<sub>2</sub>O  
274 emission factor (EF<sub>N<sub>2</sub>O</sub>) and duration of settling phase. (B) pH and volumetric nitrification rate. (C) Concentrations

275 of the major soluble nitrogen compounds. (D) Dissolved oxygen (DO) and temperature. A statistical overview of  
276 all measured variables can be found in the **SI 6**.

277 A wide range of typical environmental conditions for urine nitrification was covered during the  
278 measurement campaign (**Figure 2B to 2D**). Higher pH generally resulted in higher nitrification rates  
279 with a mean of  $860 \text{ mg-N L}^{-1} \text{ d}^{-1}$ . Due to the stable influent composition with TN concentrations of  
280 around  $3500 \text{ mg N L}^{-1}$ , the ammonium and nitrate concentrations in the reactor were fairly constant  
281 around  $1750 \text{ mg-N L}^{-1}$ . Nitrite peaks up to  $20 \text{ mg-N L}^{-1}$  were triggered either by a temporary increase in  
282 pH setpoints or a decrease in airflow leading to DO concentrations as low as  $0.4 \text{ mg L}^{-1}$  in the second  
283 half of the measurement campaign. Temperature was fairly constant with a standard deviation of  $0.4^\circ\text{C}$ .



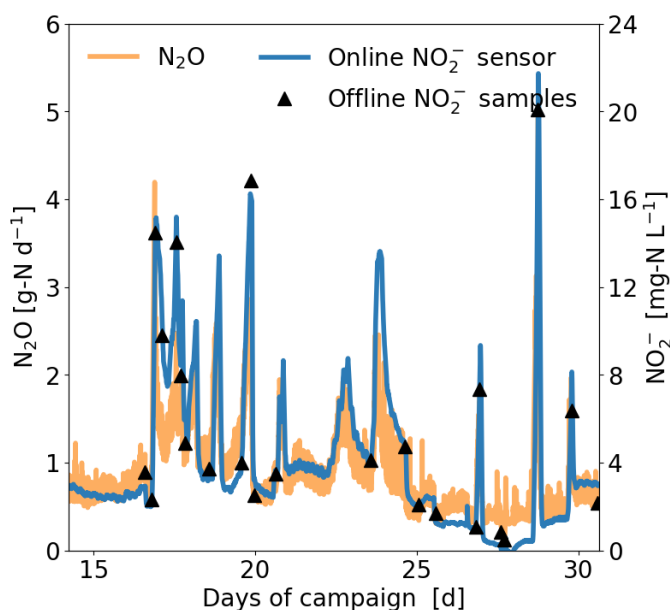
284

285 **Figure 3:**  $\text{N}_2\text{O}$  off-gas load within a fed-batch cycle for two different settling times. The dissolved oxygen (DO)  
286 concentration indicates the start and end of the settling and decant phase.

287 Within a fed-batch cycle, a significant  $\text{N}_2\text{O}$  peak occurred always after the settling and decant phase,  
288 accounting for up to 85% of the emission during a fed-batch cycle with a settling time of 30 minutes  
289 (**Figure 3**). Within less than one hour, the emissions returned to the level prior to the settling phase. A  
290 shorter settling time of 15 minutes resulted in a smaller peak in  $\text{N}_2\text{O}$  emissions and thus lower  $\text{N}_2\text{O}$   
291 emissions per fed-batch cycle, which explains the influence of the settling time. For  $\text{NO}$ , a high emission  
292 peak was also observed at the beginning of the aeration phase ( $\text{NO}$  emissions during a fed-batch cycle  
293 in **SI 7**). For further analysis, the characteristic  $\text{N}_2\text{O}$  peak in the first hour after the decant phase was



294 separated from the rest of the aerated phase for every fed-batch cycle (see **SI 8** for data processing).  
 295 Overall, the peaks at the beginning of each aeration phase were responsible for 55% of the N<sub>2</sub>O  
 296 emissions during the entire measurement campaign. The strongest correlation with the N<sub>2</sub>O peaks was  
 297 found for the settling time with a Pearson's correlation coefficient of  $r = 0.89$  ( $p < 0.05$ ) (correlations  
 298 plots in **SI 9**).



299

300 **Figure 4:** N<sub>2</sub>O emissions attributed to the aerobic activity during nitrification (excluding the emission peak in the  
 301 first hour after re-aeration). Only the data of the measurement campaign with the online nitrite sensor are shown.

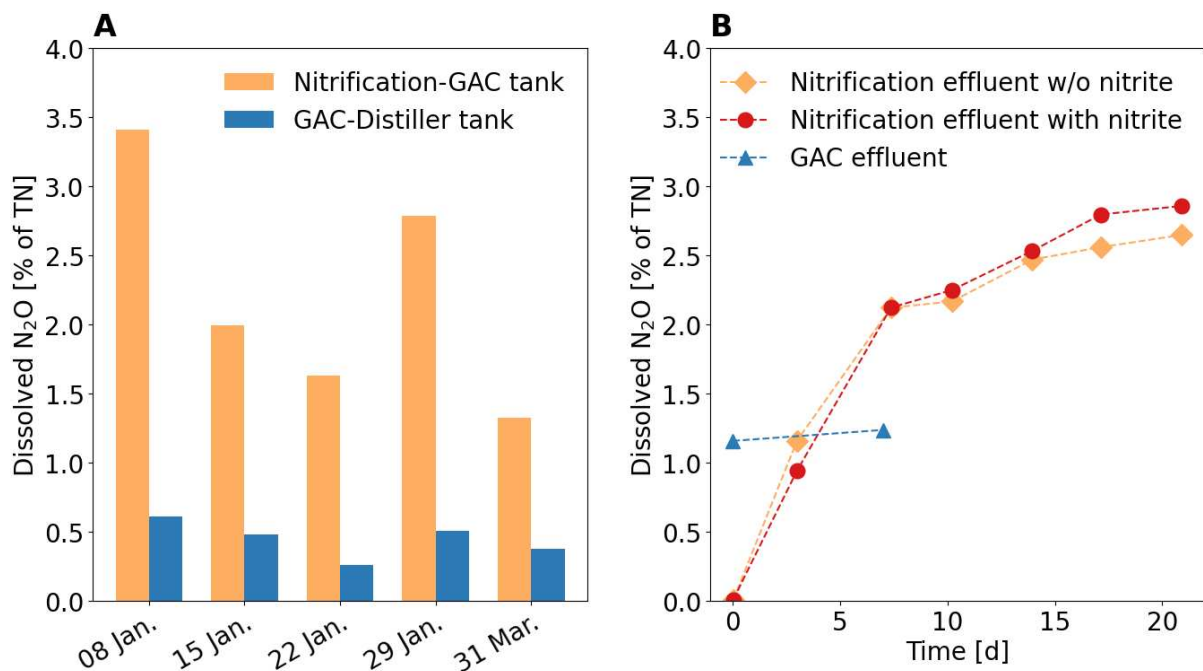
302 A strong increase in the nitrite concentration always went along with an increase in N<sub>2</sub>O emissions  
 303 during the aerated phase of the fed-batch cycle (**Figure 4**). The Pearson correlation coefficient of  
 304  $r = 0.84$  ( $p < 0.05$ ) for the nitrite relative to the N<sub>2</sub>O load was the highest correlation found for all  
 305 investigated variables (correlation plots in **SI 10**). A moderate correlation of  $r = 0.53$  ( $p < 0.05$ ) remained  
 306 for nitrite if the Pearson coefficient was calculated for the  $EF_{N_2O}$ . DO levels also affected N<sub>2</sub>O emissions  
 307 during the aerated phase. Over the entire measurement campaign, the  $EF_{N_2O}$  and the DO concentration  
 308 showed a moderate negative correlation of  $r = -0.45$  ( $p < 0.05$ ), and especially DO concentrations below  
 309  $2 \text{ mg L}^{-1}$  seem to increase N<sub>2</sub>O emissions. A temporary decrease of DO from  $3 \text{ mg L}^{-1}$  to  $1.5 \text{ mg L}^{-1}$  on  
 310 day 10 led to an increase of N<sub>2</sub>O by more than a factor of 10, which was reversible once the DO was  
 311 increased again (DO experiment in **SI 11**).

312

16

313 **3.2 N<sub>2</sub>O emissions from intermediate storage, GAC filtration and distillation**

314 Dissolved N<sub>2</sub>O concentrations of up to 90 mg-N L<sup>-1</sup>, representing 3.4% of the dissolved TN, were found  
 315 in the first intermediate storage between nitrification and GAC filtration (**Figure 5A**). The N<sub>2</sub>O fraction  
 316 had a strong linear relationship ( $R^2 = 0.83$ ) with the HRT in the storage tank (linear regression in **SI 12**).  
 317 N<sub>2</sub>O fractions were considerably lower in the second intermediate storage between GAC filtration and  
 318 distillation. Grab samples from the first intermediate storage, the influent and the effluent of the GAC,  
 319 and the second intermediate storage showed that the N<sub>2</sub>O fraction did not change during GAC filtration  
 320 (measurement in **SI 13**). The lower N<sub>2</sub>O fraction in the intermediate storage between the GAC filter and  
 321 the distiller must therefore be due to processes in this tank itself and are not a result of biological  
 322 processes in the GAC filter.



323 **Figure 5:** N<sub>2</sub>O production during intermediate storage after nitrification and GAC filtration. (A) Grab samples  
 324 from the intermediate storage. (B) Bottle experiment with nitrification effluent and GAC filtration effluent.

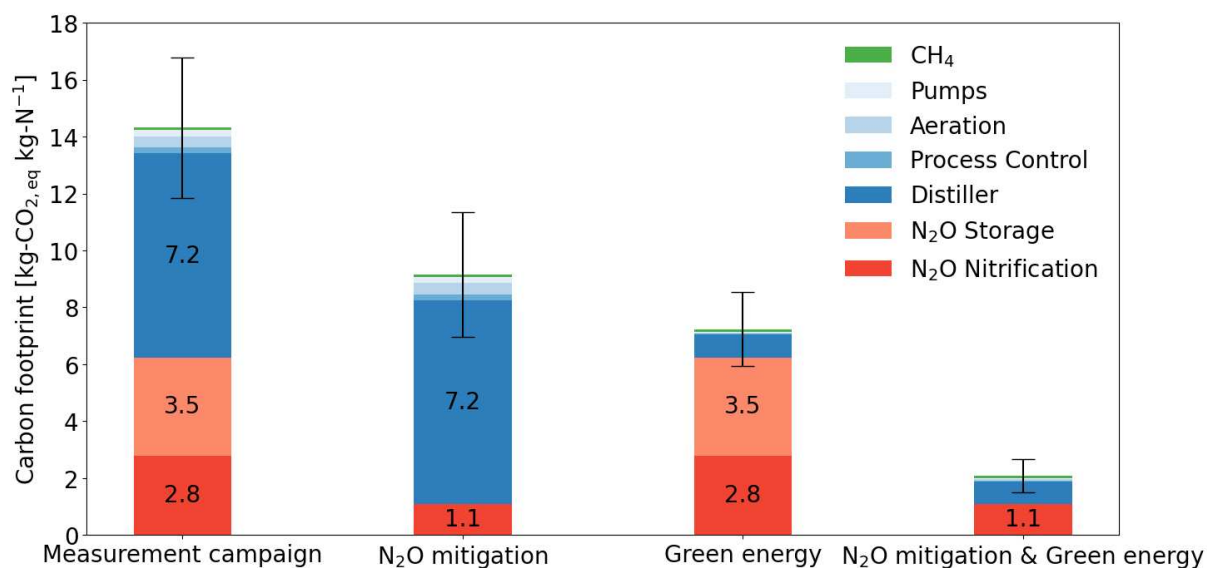
326 Nitrite concentrations did not influence N<sub>2</sub>O production during intermediate storage (**Figure 5B**). The  
 327 addition of 10 mg-N L<sup>-1</sup> had a negligible effect in the bottle experiment with the nitrification effluent.  
 328 The N<sub>2</sub>O fraction in the effluent of the nitrification reactor were 0.01% of the dissolved TN after a  
 329 settling time of 6 minutes, but increased up to 2.9% of the dissolved TN within three weeks. In contrast,  
 330 the N<sub>2</sub>O in the effluent of the GAC increased only slightly within one week.

331 The measurement campaign for the intermediate storage and the GAC were conducted during a period  
332 of comparatively low flow rates due to the limited availability of fresh urine. To obtain a representative  
333  $EF_{N_2O}$  for the main measurement campaign, the  $N_2O$  fraction was estimated using the above mentioned  
334 linear relationship between the  $N_2O$  fraction and the HRT. Based on the average HRT of 1.7 days during  
335 the main measurement campaign, a dissolved  $N_2O$  fraction of  $0.8 \pm 0.3\%$  of the dissolved TN was  
336 estimated for the first intermediate storage.

### 337 **3.3 Operational carbon footprint**

338 Overall, the operational carbon footprint during the main measurement campaign was  
339  $14.3 \pm 2.5 \text{ kg-CO}_{2,\text{eq}} \text{ kg-N}^{-1}$  using the European electricity mix, with  $N_2O$  accounting for about 45% of  
340 carbon footprint (**Figure 6**). For  $N_2O$  emissions during intermediate storage, the estimated  $EF_{N_2O}$  of  
341  $0.8 \pm 0.3\%$  was used, assuming that all dissolved  $N_2O$  from the first intermediate storage is volatilized  
342 at the latest in the distiller and that no  $N_2O$  is produced after GAC filtration. The distillation process was  
343 the largest contributor to the carbon footprint. In contrast, the carbon footprint of the aeration, pumps  
344 and process control accounted for only a small portion of the total footprint (see details of energy  
345 calculation in **SI 4**). Direct  $CH_4$  emissions were also negligible, with a carbon equivalent of  
346  $0.02 \pm 0.01 \text{ kg-CO}_{2,\text{eq}} \text{ kg-N}^{-1}$  for the collection tanks (details in **SI 14**) and of  
347  $0.07 \pm 0.03 \text{ kg-CO}_{2,\text{eq}} \text{ kg-N}^{-1}$  (timeline in **SI 15**) for the nitrification. Direct  $CO_2$  emissions from the  
348 biological process had a strong linear relationship with the nitrogen in the influent, with a ratio of

349 2 kg-CO<sub>2</sub> kg-N<sup>-1</sup> (timeline in **SI 16**), but because direct CO<sub>2</sub> emissions are biogenic, they were not  
 350 included in the carbon footprint calculation.



351  
 352 **Figure 6:** Operational carbon footprint for the measurement campaign using a European electricity mix, a N<sub>2</sub>O  
 353 mitigation scenario, a green energy mix scenario, and a combination of both scenarios. Error bars represent ± one  
 354 standard deviation. A table with all values including the uncertainties can be found in **SI 17**.

355 To investigate the influence of potential carbon reduction strategies, different scenarios were compared  
 356 (**Figure 6**). In the N<sub>2</sub>O mitigation scenario, N<sub>2</sub>O emissions during nitrification were assumed to be  
 357 reduced by completely avoiding periods without aeration and by keeping nitrite concentrations below  
 358 5 mg-N L<sup>-1</sup> resulting in an EF<sub>N<sub>2</sub>O</sub> of 0.26 ± 0.13% of the nitrogen load (timeline in **SI 18**). Furthermore,  
 359 it was assumed that the N<sub>2</sub>O emissions from intermediate storage can be completely avoided by directly  
 360 feeding the GAC filter. This is possible if the GAC loading capacity is higher than the observed  
 361 maximum loading rate to the nitrification, as it was the case for the measurement campaign. In the green  
 362 energy mix scenario, N<sub>2</sub>O emissions remained unchanged, and the current European electricity mix was  
 363 replaced with the green energy mix. Last but not least, both reduction strategies were combined. The  
 364 N<sub>2</sub>O mitigation scenario and the green energy mix scenario strongly reduced the carbon footprint by  
 365 about 35% to 9.2 ± 2.2 kg-CO<sub>2,eq</sub> kg-N<sup>-1</sup> and 50% to 7.2 ± 1.3 kg-CO<sub>2,eq</sub> kg-N<sup>-1</sup>, respectively. A  
 366 combination of both strongly reduced the carbon footprint by 85% down to 2.1 ± 0.6 kg-CO<sub>2,eq</sub> kg-N<sup>-1</sup>.

## 367 **4 Discussion**

### 368 **4.1 Sources and influencing factors of N<sub>2</sub>O emissions**

369 The average EF<sub>N<sub>2</sub>O</sub> of 0.7% for urine nitrification falls well within the range of 0.01% to 2% suggested  
370 for mainstream nitrification processes,<sup>16</sup> and is lower than the average EF<sub>N<sub>2</sub>O</sub> of 1.9% reported by Gruber  
371 et al.<sup>15</sup> for three long-term measurement campaign of mainstream nitrification. Comparing urine  
372 nitrification with the treatment of digester supernatant, which is more similar in terms of concentrations,  
373 the measured EF<sub>N<sub>2</sub>O</sub> is even at the lower end of the range from 0.2% to 5.1% reported for sidestream  
374 reactors.<sup>16</sup>

375 DO and nitrite were identified as the most important factors influencing N<sub>2</sub>O emissions during  
376 nitrification. In particular, long anoxic phases or phases with very low DO (e.g. settling phase) lead to  
377 high N<sub>2</sub>O emissions. The strong dependence of N<sub>2</sub>O emissions from the settling time indicates that N<sub>2</sub>O  
378 was mostly produced during the unaerated phases and then was stripped once aeration started, resulting  
379 in a dominant N<sub>2</sub>O peak. Similar N<sub>2</sub>O peaks in the beginning of the aerated phase were also observed  
380 by Stenstrom et al.<sup>39</sup> for sidestream nitrification and denitrification or by Gabarro et al.<sup>40</sup> for partial  
381 nitrification of as landfill leachate. Nitrifier denitrification or heterotrophic denitrification are presumably  
382 the predominant pathways during the settling and decant phase, also indicated by the peak in NO  
383 concentration, which is an intermediate of the denitrification pathways.<sup>41</sup> High N<sub>2</sub>O emissions during  
384 the aerated phase were concomitantly observed with high nitrite concentrations in the reactor. This  
385 positive correlation between nitrite concentration and N<sub>2</sub>O emissions has been shown in several other  
386 publications.<sup>32, 42</sup> As the N<sub>2</sub>O emissions during the aerated phase correlated with the nitrite  
387 concentrations, a nitrifier denitrification or heterotrophic denitrification pathway is very likely.<sup>16</sup>

388 The EF<sub>N<sub>2</sub>O</sub> in the intermediate storage after the nitrification was estimated to 0.8%, which more than  
389 doubled the N<sub>2</sub>O emissions of the overall treatment chain. During periods of very low flow rates, either  
390 due to limited urine availability or slow nitrification rates, N<sub>2</sub>O production from the intermediate storage  
391 would be even higher. Significant N<sub>2</sub>O emissions are known to occur in secondary clarifiers of  
392 WWTP,<sup>43-44</sup> but the emissions from the second clarifiers strongly correlated with the emissions from the

393 biological treatment, indicating that the N<sub>2</sub>O from WWTP secondary clarifiers was already produced in  
394 the biological nitrification and denitrification step. In contrast, the dissolved N<sub>2</sub>O measurements from  
395 the urine treatment chain clearly showed that the N<sub>2</sub>O was produced during intermediate storage.

396 The HRT in the intermediate storage between nitrification and GAC filtration was identified to be the  
397 most important factor for N<sub>2</sub>O production. Similar to the settling and decant phases, DO concentrations  
398 were very low in the intermediate storage, which most likely led to nitrifier denitrification and  
399 heterotrophic denitrification. Although the biomass concentration in the storage tank is much lower than  
400 in the reactor, the longer retention time of at least one day compared to the settling time of max.  
401 30 minutes led to high N<sub>2</sub>O production. After the GAC filtration the N<sub>2</sub>O production seems to stop (see  
402 **Figure 5B**), which could be related to the removal of residual COD or removal of active biomass in the  
403 filter.<sup>10</sup> In the second intermediate storage the N<sub>2</sub>O concentration was around 80% lower than in the first  
404 intermediate storage. Since no removal was observed in the GAC, and the bottle experiment with the  
405 GAC effluent did not reveal any N<sub>2</sub>O sink due to denitrification, it is very likely that the decrease in  
406 N<sub>2</sub>O concentration in the second intermediate storage was caused by N<sub>2</sub>O volatilization. Although the  
407 tank was covered, a liquid-air exchange of around 350 L occurred each time the distillation was turned  
408 on, which increased N<sub>2</sub>O volatilization. N<sub>2</sub>O most likely also volatilized in the first intermediate storage  
409 tank, but the volatilization should be much lower because the volume was more constant and therefore  
410 less liquid-air exchange occurred. Nevertheless, further studies would be needed to determine the  
411 amount of N<sub>2</sub>O leaking from the intermediate storage and the exact cause of the lower N<sub>2</sub>O concentration  
412 in the second intermediate storage.

413 The emission factor for the whole urine fertilizer production was estimated at 1.5%. For comparison,  
414 Gruber (2021)<sup>15</sup> calculated an emission factor of 2% for a model WWTP where 60% of emissions came  
415 from from the mainstream nitrification and denitrification and secondary clarifier, and 40% from the  
416 sidestream treatment and sludge incineration.

417

418

## 419        **4.2 N<sub>2</sub>O mitigation strategies**

420    Anoxic conditions and conditions with very low DO must be avoided during urine nitrification, e.g. by  
421    reducing the settling time during the fed-batch cycle as shown in **Figure 2** and **Figure 3**. If the settling  
422    time is reduced, the time in which N<sub>2</sub>O can be produced is reduced. However, the minimum settling  
423    time must be chosen based on the sludge settling characteristics to avoid undesirable biomass loss. A  
424    settling time around 6 minutes, as applied in this study, should be appropriate. Another option is to  
425    operate a reactor setup without a settling phase, such as a membrane bioreactor (MBR) or a biofilm  
426    system. However, system changes require additional studies on N<sub>2</sub>O emissions, because other pathways  
427    of N<sub>2</sub>O formation could occur. The use of biofilm-based nitrification systems could result in anoxic  
428    zones within the biofilm and promote denitrification and N<sub>2</sub>O production.<sup>45</sup> Based on this study, the DO  
429    concentration during the aerated phase should probably be maintained above 2 mg L<sup>-1</sup>. Similar  
430    guidelines have been proposed for centralized wastewater treatment,<sup>23</sup> but while DO concentrations  
431    above 2 mg L<sup>-1</sup> are difficult to achieve in mainstream treatment, high DO concentrations during urine  
432    nitrification are feasible.

433    In partial urine nitrification, high nitrite concentrations can be avoided by controlling nitrification using  
434    continuous nitrite monitoring with an electrochemical nitrite sensor as proposed in Britschgi et al.<sup>35</sup>) or  
435    with ultraviolet spectrophotometry.<sup>46</sup> Based on this study, an upper limit for nitrite of 5 mg-N L<sup>-1</sup> might  
436    be suitable, which is more conservative than the upper limit of 12 to 30 mg-N L<sup>-1</sup> proposed by Britschgi  
437    et al.<sup>35</sup> for stable partial urine nitrification, or the upper limit of 20 mg-N L<sup>-1</sup> applied during the  
438    measurement campaign. Another approach to mitigate N<sub>2</sub>O emissions might be to separate the treatment  
439    of organics from nitrification. This could reduce the abundance of heterotrophic bacteria and of soluble  
440    organics in the reactor, thus reducing denitrification. Degradation of organics prior to urine nitrification  
441    has been tested<sup>47</sup>), but the N<sub>2</sub>O emissions from these systems have yet to be determined. In the long  
442    term, off-gas treatment could become an option since the off-gas can be easily captured, but cheap and  
443    suitable catalysts for decentralized treatment are not yet available.

444    To mitigate N<sub>2</sub>O production during intermediate storage, the storage duration before GAC filtration  
445    should be minimized. The most effective way to do this, would be to reduce the working volume of the

446 storage tank prior to the GAC filter or to directly feed the GAC filter, which could potentially fully  
447 mitigate the N<sub>2</sub>O production during intermediate storage. This is possible as long as the maximum  
448 observed flow rate in the nitrification is less than the dimensioned flow rate through the GAC column,  
449 as it was the case in the studied urine fertilizer production. In addition, biomass overflow from the  
450 nitrification step should be minimized, as this adds active biomass and organic substrate to the storage  
451 tank. While a longer settling time would result in a better solid-liquid separation and therefore less  
452 biomass overflow, it would also result in higher N<sub>2</sub>O emissions during nitrification, so a different  
453 approach should be taken to minimize the amount of biomass in the storage tank. For example, the  
454 biomass at the bottom of the storage tank could be pumped back to the nitrification reactor, or biomass  
455 could be retained in the reactor using a MBR, with the added benefit of avoiding anoxic conditions in  
456 the bioreactor. Another option would be to slightly aerate the storage tank to avoid anoxic conditions,  
457 but this could lead to a drop in pH and the release of harmful NO due the growth of acid-tolerant AOB.<sup>48</sup>  
458 Especially for life support systems in space, N<sub>2</sub>O and NO emissions need to be minimized because they  
459 can become a potential health hazards in closed systems.<sup>7</sup>

### 460 **4.3 Carbon footprint of urine fertilizer production**

461 Direct N<sub>2</sub>O emissions and indirect CO<sub>2</sub> emissions from the distiller are the main contributors to the  
462 carbon footprint. Concentrating the nutrients in the treated urine with the distiller, to reduce the volume  
463 for easier transport and storage, is energy-intensive. If the fertilizer is applied where it is produced (e.g.  
464 urban farming), distillation would become obsolete and a more energy-efficient pasteurization step  
465 would be sufficient to kill the pathogens. Since the energy required for aeration is almost negligible, the  
466 trade-off between the N<sub>2</sub>O mitigation due to higher DO and the increased energy demand of aeration is  
467 small. In Fumasoli et al.<sup>27</sup> the energy demand for aeration during urine nitrification was at least six times  
468 larger than during the measurement campaign because higher airflow rates were applied to ensure  
469 sufficient mixing in the moving bed biofilm reactor, which resulted in constantly high DO  
470 concentrations above 7 mg L<sup>-1</sup>. Such high airflow rates and DO concentrations were not required during  
471 the measurement campaign. Mitigation of N<sub>2</sub>O emissions had a smaller impact than changing the energy  
472 mix towards a greener energy mix, which is different than for WWTPs where N<sub>2</sub>O mitigation has the



473 largest impact on the carbon footprint.<sup>49</sup> Nevertheless, the proposed simple N<sub>2</sub>O mitigation measures  
474 should be pursued, especially as they should not conflict with process stability.

475 The N<sub>2</sub>O emissions and the operational carbon footprints derived in this study can be used as part of a  
476 comprehensive LCA that compares urine fertilizer production with centralized removal of the nutrients  
477 contained in urine and synthetic fertilizer production. For a holistic comparison, the footprint associated  
478 with reactor and sewer components and N<sub>2</sub>O emissions from different fertilizers applied to agricultural  
479 fields<sup>50</sup> must be considered, which was beyond the scope of this study. In addition, it should be taken  
480 into account that on-site urine treatment could for example allow for a higher heat recovery at household  
481 level,<sup>51</sup> avoid GHG emissions in the sewer,<sup>52</sup> save flushing water,<sup>19</sup> and enable local fertilizer  
482 production<sup>19</sup>.

483

484        **5 Conclusions**

- 485        • N<sub>2</sub>O emissions during urine nitrification are in the same range as for mainstream nitrification,  
486                despite higher nitrite concentrations and higher ammonium oxidation rates.
- 487        • N<sub>2</sub>O emissions during urine nitrification can effectively be mitigated by avoiding phases with  
488                low or no DO (e.g. settling phases) and nitrite concentrations above 5 mg-N L<sup>-1</sup>.
- 489        • N<sub>2</sub>O production during intermediate storage between nitrification and GAC filtration doubles  
490                the N<sub>2</sub>O emissions of the treatment chain but can be strongly mitigated by directly feeding  
491                nitrified urine to the GAC filtration without intermediate storage.
- 492        • Direct N<sub>2</sub>O emissions and indirect CO<sub>2</sub> emissions from distillation are major contributors to the  
493                carbon footprint, hence it is worth to mitigate N<sub>2</sub>O emissions and opt for a green electricity mix.

494

## 495 **Supporting information**

496 The supporting information is available free of charge at <http://pubs.acs.org>: Details on the energy  
497 calculations, additional data from the urine treatment system, and supplementary results from the N<sub>2</sub>O,  
498 NO, and CH<sub>4</sub> measurement campaigns (PDF).

## 499 **Declaration of Competing Interests**

500 The authors declare the following financial interests/personal relationships, which may be considered  
501 as potential competing interests: Kai M. Udert is co-owner of the Eawag spin-off Vuna Ltd. The  
502 company uses biological and physical processes for nutrient recovery from urine. The study was not  
503 influenced by the relationship of Kai M. Udert with Vuna Ltd.

## 504 **Acknowledgements**

505 This article has been made possible through the author's involvement in the MELiSSA project, the life  
506 support system research program from the European Space Agency (ESA)  
507 ([http://www.esa.int/Our\\_Activities/Space\\_Engineering\\_Technology/Melissa](http://www.esa.int/Our_Activities/Space_Engineering_Technology/Melissa)). The authors would like  
508 to acknowledge the MELiSSA foundation to support Valentin Faust via the POMP2 (Pool of MELiSSA  
509 PhD) program. Ramon Ganigué gratefully acknowledges support from BOF startkrediet  
510 (BOF19/STA/044). The authors would like to thank Patrick Kathriner (Eawag) and the department of  
511 Surface Waters Research and Management at Eawag for the excellent support with dissolved N<sub>2</sub>O  
512 measurements. We would also like to thank Sylvia Richter (Eawag) and Karin Rottermann (Eawag) for  
513 helping with the chemical analysis and Marco Kipf (Eawag), Bettina Sterkele (Eawag), Nadège de  
514 Chambrier (Vuna Ltd) and Bastian Etter (Vuna Ltd) for technical support and scientific advice.

- 516 1. Tchobanoglous, G.; Stensel, H. D.; Tsuchihashi, R.; Burton, F. L.; Abu-Orf, M.; Bowden, G.;  
517 Pfrang, W.; Metcalf & Eddy, *Wastewater engineering : treatment and resource recovery*. Fifth edition  
518 / ed.; McGraw-Hill Education: New York, NY, 2014; p xxix, 2018 pages.
- 519 2. Leigh, G. J., Haber-Bosch and Other Industrial Processes. In *Catalysts for Nitrogen Fixation:  
520 Nitrogenases, Relevant Chemical Models and Commercial Processes*, Smith, B. E.; Richards, R. L.;  
521 Newton, W. E., Eds. Springer Netherlands: Dordrecht, 2004; pp 33-54.
- 522 3. Larsen, T. A.; Riechmann, M. E.; Udert, K. M., State of the art of urine treatment  
523 technologies: A critical review. *Water Res X* **2021**, *13*, 100114.
- 524 4. Hoffmann, S.; Feldmann, U.; Bach, P. M.; Binz, C.; Farrelly, M.; Frantzeskaki, N.; Hiessl, H.;  
525 Inauen, J.; Larsen, T. A.; Lienert, J.; Londong, J.; Luthi, C.; Maurer, M.; Mitchell, C.; Morgenroth, E.;  
526 Nelson, K. L.; Scholten, L.; Truffer, B.; Udert, K. M., A Research Agenda for the Future of Urban  
527 Water Management: Exploring the Potential of Nongrid, Small-Grid, and Hybrid Solutions. *Environ  
528 Sci Technol* **2020**, *54* (9), 5312-5322.
- 529 5. Larsen, T. A.; Udert, K. M.; Lienert, J., *Source Separation and Decentralization for  
530 Wastewater Management*. IWA Publishing: London, UK, 2013; p 491.
- 531 6. Steffen, W.; Richardson, K.; Rockstrom, J.; Cornell, S. E.; Fetzer, I.; Bennett, E. M.; Biggs,  
532 R.; Carpenter, S. R.; de Vries, W.; de Wit, C. A.; Folke, C.; Gerten, D.; Heinke, J.; Mace, G. M.;  
533 Persson, L. M.; Ramanathan, V.; Reyers, B.; Sorlin, S., Sustainability. Planetary boundaries: guiding  
534 human development on a changing planet. *Science* **2015**, *347* (6223), 1259855.
- 535 7. Clauwaert, P.; Muys, M.; Alloul, A.; De Paepe, J.; Luther, A.; Sun, X.; Ilgrande, C.;  
536 Christiaens, M. E. R.; Hu, X.; Zhang, D.; Lindeboom, R. E. F.; Sas, B.; Rabaey, K.; Boon, N.; Ronsse,  
537 F.; Geelen, D.; Vlaeminck, S. E., Nitrogen cycling in Bioregenerative Life Support Systems:  
538 Challenges for waste refinery and food production processes. *Progress in Aerospace Sciences* **2017**,  
539 *91*, 87-98.
- 540 8. Verbeelen, T.; Leys, N.; Ganigue, R.; Mastroleo, F., Development of Nitrogen Recycling  
541 Strategies for Bioregenerative Life Support Systems in Space. *Front Microbiol* **2021**, *12*, 700810.
- 542 9. Fumasoli, A. Nitrification of Urine as pretreatment for nutrient recovery ETH Zurich, 2016.
- 543 10. Kopping, I.; Mc Ardell, C. S.; Borowska, E.; Bohler, M. A.; Udert, K. M., Removal of  
544 pharmaceuticals from nitrified urine by adsorption on granular activated carbon. *Water Res X* **2020**, *9*,  
545 100057.
- 546 11. Environmental management — Life cycle assessment — Requirements and guidelines. ISO  
547 14044. British Standards Institution: London, 2006.
- 548 12. Daelman, M. R.; van Voorthuizen, E. M.; van Dongen, L. G.; Volcke, E. I.; van Loosdrecht,  
549 M. C., Methane and nitrous oxide emissions from municipal wastewater treatment - results from a  
550 long-term study. *Water Sci Technol* **2013**, *67* (10), 2350-5.
- 551 13. Schreiber, F.; Wunderlin, P.; Udert, K. M.; Wells, G. F., Nitric oxide and nitrous oxide  
552 turnover in natural and engineered microbial communities: biological pathways, chemical reactions,  
553 and novel technologies. *Front Microbiol* **2012**, *3*, 372.
- 554 14. Conthe, M.; Lycus, P.; Arntzen, M. O.; Ramos da Silva, A.; Frostegard, A.; Bakken, L. R.;  
555 Kleerebezem, R.; van Loosdrecht, M. C. M., Denitrification as an N<sub>2</sub>O sink. *Water Res* **2019**, *151*,  
556 381-387.
- 557 15. Gruber, W.; von Kanel, L.; Vogt, L.; Luck, M.; Biolley, L.; Feller, K.; Moosmann, A.;  
558 Krahenbuhl, N.; Kipf, M.; Loosli, R.; Vogel, M.; Morgenroth, E.; Braun, D.; Joss, A., Estimation of  
559 countrywide N<sub>2</sub>O emissions from wastewater treatment in Switzerland using long-term monitoring  
560 data. *Water Res X* **2021**, *13*, 100122.
- 561 16. Vasilaki, V.; Massara, T. M.; Stanchev, P.; Fatone, F.; Katsou, E., A decade of nitrous oxide  
562 (N<sub>2</sub>O) monitoring in full-scale wastewater treatment processes: A critical review. *Water Res* **2019**,  
563 *161*, 392-412.
- 564 17. Bartram, D.; Short, M. D.; Ebie, Y.; Farkaš, J.; Gueguen, C.; Peters, G. M.; Zanzottera, N. M.;  
565 Karthik, M. *2019 Refinement to the 2006 IPCC Guidelines for National Greenhouse Gas Inventories -  
566 5.6 Wastewater treatment and discharge*; IPCC: Switzerland, 2019.
- 567 18. Martin, T. L'urine humaine en agriculture : des filières variées pour contribuer à une  
568 fertilisation azotée durable. Cumulative thesis, Université Paris-Saclay, 2020.

- 569 19. Hilton, S. P.; Keoleian, G. A.; Daigger, G. T.; Zhou, B.; Love, N. G., Life Cycle Assessment  
570 of Urine Diversion and Conversion to Fertilizer Products at the City Scale. *Environ Sci Technol* **2021**,  
571 55 (1), 593-603.
- 572 20. Igos, E.; Besson, M.; Navarrete Gutierrez, T.; Bisinella de Faria, A. B.; Benetto, E.; Barna, L.;  
573 Ahmadi, A.; Sperandio, M., Assessment of environmental impacts and operational costs of the  
574 implementation of an innovative source-separated urine treatment. *Water Res* **2017**, 126, 50-59.
- 575 21. Kavvada, O.; Tarpeh, W. A.; Horvath, A.; Nelson, K. L., Life-Cycle Cost and Environmental  
576 Assessment of Decentralized Nitrogen Recovery Using Ion Exchange from Source-Separated Urine  
577 through Spatial Modeling. *Environ Sci Technol* **2017**, 51 (21), 12061-12071.
- 578 22. Spangberg, J.; Tidaker, P.; Jonsson, H., Environmental impact of recycling nutrients in human  
579 excreta to agriculture compared with enhanced wastewater treatment. *Sci Total Environ* **2014**, 493,  
580 209-19.
- 581 23. Massara, T. M.; Malamis, S.; Guisasola, A.; Baeza, J. A.; Noutsopoulos, C.; Katsou, E., A  
582 review on nitrous oxide (N<sub>2</sub>O) emissions during biological nutrient removal from municipal  
583 wastewater and sludge reject water. *Sci Total Environ* **2017**, 596, 106-123.
- 584 24. Adouani, N.; Limousy, L.; Lendormi, T.; Sire, O., N<sub>2</sub>O and NO emissions during wastewater  
585 denitrification step: Influence of temperature on the biological process,. *Comptes Rendus Chimie*  
586 **2015**, 18 (1), 15-22.
- 587 25. Vasilaki, V.; Volcke, E. I. P.; Nandi, A. K.; van Loosdrecht, M. C. M.; Katsou, E., Relating  
588 N<sub>2</sub>O emissions during biological nitrogen removal with operating conditions using multivariate  
589 statistical techniques. *Water Res* **2018**, 140, 387-402.
- 590 26. Udert, K. M.; Larsen, T. A.; Biebow, M.; Gujer, W., Urea hydrolysis and precipitation  
591 dynamics in a urine-collecting system. *Water Res* **2003**, 37 (11), 2571-2582.
- 592 27. Fumasoli, A.; Etter, B.; Sterkele, B.; Morgenroth, E.; Udert, K. M., Operating a pilot-scale  
593 nitrification/distillation plant for complete nutrient recovery from urine. *Water Sci Technol* **2016**, 73  
594 (1), 215-22.
- 595 28. Udert, K. M.; Larsen, T. A.; Gujer, W., Fate of major compounds in source-separated urine.  
596 *Water Sci Technol* **2006**, 54 (11-12), 413-420.
- 597 29. Gruber, W.; Villez, K.; Kipf, M.; Wunderlin, P.; Siegrist, H.; Vogt, L.; Joss, A., N<sub>2</sub>O emission  
598 in full-scale wastewater treatment: Proposing a refined monitoring strategy. *Sci Total Environ* **2020**,  
599 699, 134157.
- 600 30. Woszczyk, M.; Schubert, C. J., Greenhouse gas emissions from Baltic coastal lakes. *Sci Total*  
601 *Environ* **2021**, 755 (Pt 2), 143500.
- 602 31. Weiss, R. F.; Price, B. A., Nitrous oxide solubility in water and seawater. *Marine Chemistry*  
603 **1980**, 8 (4), 347-359.
- 604 32. Peng, L.; Ni, B. J.; Ye, L.; Yuan, Z., The combined effect of dissolved oxygen and nitrite on  
605 N<sub>2</sub>O production by ammonia oxidizing bacteria in an enriched nitrifying sludge. *Water Res* **2015**, 73,  
606 29-36.
- 607 33. Galle, M.; Agar, D. W.; Watzenberger, O., Thermal N<sub>2</sub>O decomposition in regenerative heat  
608 exchanger reactors. *Chemical Engineering Science* **2001**, 56 (4), 1587-1595.
- 609 34. Udert, K. M.; Wachter, M., Complete nutrient recovery from source-separated urine by  
610 nitrification and distillation. *Water Res* **2012**, 46 (2), 453-64.
- 611 35. Britschgi, L.; Villez, K.; Schrems, P.; Udert, K. M., Electrochemical nitrite sensing for urine  
612 nitrification. *Water Res X* **2020**, 9, 100055.
- 613 36. Doorn, M. R. J.; Towprayoon, S.; Vieira, S. M. M.; Irving, W.; Palmer, C.; Pipatti, R.; Wang,  
614 C. *2006 IPCC Guidelines for National Greenhouse Gas Inventories - 5.6 Wastewater treatment and*  
615 *discharge*; IPCC: Switzerland, 2006.
- 616 37. IPCC, Climate Change 2014: Synthesis Report. Contribution of Working Groups I, II and III  
617 to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change, p. 151, IPCC,  
618 Geneva, Switzerland. **2014**.
- 619 38. Greenhouse gas emission intensity of electricity generation by country.  
620 [https://www.eea.europa.eu/data-and-maps/daviz/co2-emission-intensity-9#tab-](https://www.eea.europa.eu/data-and-maps/daviz/co2-emission-intensity-9#tab-googlechartid_googlechartid_googlechartid_googlechartid_chart_11111)  
621 [googlechartid googlechartid googlechartid googlechartid chart 11111](https://www.eea.europa.eu/data-and-maps/daviz/co2-emission-intensity-9#tab-googlechartid_googlechartid_googlechartid_googlechartid_chart_11111) (accessed 08.11.2021).
- 622 39. Stenstrom, F.; Tjus, K.; la Cour Jansen, J., Oxygen-induced dynamics of nitrous oxide in  
623 water and off-gas during the treatment of digester supernatant. *Water Sci Technol* **2014**, 69 (1), 84-91.

- 624 40. Gabarro, J.; Gonzalez-Carcamo, P.; Ruscalleda, M.; Ganigue, R.; Gich, F.; Balaguer, M. D.;  
625 Colprim, J., Anoxic phases are the main N<sub>2</sub>O contributor in partial nitrification reactors treating high  
626 nitrogen loads with alternate aeration. *Bioresour Technol* **2014**, *163*, 92-9.
- 627 41. Schulthess, R. v.; Gujer, W., Release of nitrous oxide (N<sub>2</sub>O) from denitrifying activated  
628 sludge: Verification and application of a mathematical model. *Water Res* **1996**, *30* (3), 521-530.
- 629 42. Daelman, M. R. J.; van Voorthuizen, E. M.; van Dongen, U.; Volcke, E. I. P.; van Loosdrecht,  
630 M. C. M., Seasonal and diurnal variability of N<sub>2</sub>O emissions from a full-scale municipal wastewater  
631 treatment plant. *Sci Total Environ* **2015**, *536*, 1-11.
- 632 43. Foley, J.; de Haas, D.; Yuan, Z.; Lant, P., Nitrous oxide generation in full-scale biological  
633 nutrient removal wastewater treatment plants. *Water Res* **2010**, *44* (3), 831-44.
- 634 44. Mikola, A.; Heinonen, M.; Kosonen, H.; Leppanen, M.; Rantanen, P.; Vahala, R., N<sub>2</sub>O  
635 emissions from secondary clarifiers and their contribution to the total emissions of the WWTP. *Water*  
636 *Sci Technol* **2014**, *70* (4), 720-8.
- 637 45. Sabba, F.; Terada, A.; Wells, G.; Smets, B. F.; Nerenberg, R., Nitrous oxide emissions from  
638 biofilm processes for wastewater treatment. *Appl Microbiol Biotechnol* **2018**, *102* (22), 9815-9829.
- 639 46. Masic, A.; Santos, A. T. L.; Etter, B.; Udert, K. M.; Villez, K., Estimation of nitrite in source-  
640 separated nitrified urine with UV spectrophotometry. *Water Res* **2015**, *85*, 244-254.
- 641 47. De Paepe, J.; De Paepe, K.; Godia, F.; Rabaey, K.; Vlaeminck, S. E.; Clauwaert, P., Bio-  
642 electrochemical COD removal for energy-efficient, maximum and robust nitrogen recovery from urine  
643 through membrane aerated nitrification. *Water Res* **2020**, *185*, 116223.
- 644 48. Fumasoli, A.; Burgmann, H.; Weissbrodt, D. G.; Wells, G. F.; Beck, K.; Mohn, J.;  
645 Morgenroth, E.; Udert, K. M., Growth of Nitrosococcus-Related Ammonia Oxidizing Bacteria  
646 Coincides with Extremely Low pH Values in Wastewater with High Ammonia Content. *Environ Sci*  
647 *Technol* **2017**, *51* (12), 6857-6866.
- 648 49. Gruber, W. Long-term N<sub>2</sub>O emission monitoring in biological wastewater treatment: methods,  
649 applications and relevance. Cumulative thesis, ETH Zurich, Zurich, 2021.
- 650 50. Halbert-Howard, A.; Hafner, F.; Karlowsky, S.; Schwarz, D.; Krause, A., Evaluating recycling  
651 fertilizers for tomato cultivation in hydroponics, and their impact on greenhouse gas emissions.  
652 *Environ Sci Pollut Res Int* **2021**, *28* (42), 59284-59303.
- 653 51. Larsen, T. A., CO<sub>2</sub>-neutral wastewater treatment plants or robust, climate-friendly  
654 wastewater management? A systems perspective. *Water Res* **2015**, *87*, 513-21.
- 655 52. Eijo-Río, E.; Petit-Boix, A.; Villalba, G.; Suárez-Ojeda, M. E.; Marin, D.; Amores, M. J.;  
656 Aldea, X.; Rieradevall, J.; Gabarrell, X., Municipal sewer networks as sources of nitrous oxide,  
657 methane and hydrogen sulphide emissions: A review and case studies. *J Environ Chem Eng* **2015**, *3*  
658 (3), 2084-2094.

659