University of South Australia

Dissolved methane in the influent of three Australian wastewater treatment plants fed by gravity sewers

This is the peer reviewed author accepted manuscript (post print) version of a published work that appeared in final form in:

Short, Michael D, Daikeler, Alexander, Wallis, Kirsten, Peirson, William L & Peters, Gregory M 2017 'Dissolved methane in the influent of three Australian wastewater treatment plants fed by gravity sewers' Science of the total environment, vol. 599-600, pp. 85-93

This output may not exactly replicate the final published authoritative version for which the publisher owns copyright. It is not the copy of record. This output may be used for non-commercial purposes. This version is licensed under a Creative Commons CC-BY-NC-ND 4.0 license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

The final definitive published version (version of record) is available at:
https://doi.org/10.1016/j.scitotenv.2017.04.152

Persistent link to the Research Outputs Repository record:
http://researchoutputs.unisa.edu.au/11541.2/126876

General Rights: Copyright and moral rights for the publications made accessible in the Research Outputs Repository are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognize and abide by the legal requirements associated with these rights.

- Users may download and print one copy for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the persistent link identifying the publication in the Research Outputs Repository

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

https://search.ror.unisa.edu.au

Dissolved methane in the influent of three Australian wastewater treatment plants fed by gravity sewers

Michael D. Short[a,b,c]*, Alexander Daikeler[c,d], Kirsten Wallis[c], William L. Peirson[c], Gregory M. Peters[e]

[a] School of Natural and Built Environments, University of South Australia, Mawson Lakes, South Australia 5095, Australia

[b] Future Industries Institute, University of South Australia, Mawson Lakes, 5095, South Australia, Australia

[c] School of Civil and Environmental Engineering, The University of New South Wales, Sydney, New South Wales 2052, Australia

[d] Institute for Energy Systems and Technology, Technische Universität Darmstadt, 64289 Darmstadt, Germany

[e] Department of Chemistry and Chemical Engineering, Chalmers University of Technology, 412 96 Gothenburg, Sweden

*Corresponding author. Tel.: +61 8 8302 3496; E-mail address: michael.short@unisa.edu.au (M.D. Short).

Abstract

Methane (CH_4) is an important anthropogenic greenhouse gas and a by-product of urban sewage management. In recent years and contrary to international (IPCC) consensus, pressurised (anaerobic) sewers were identified as important CH_4 sources, yet relatively little remains known regarding the role of gravity sewers in CH_4 production and conveyance. Here we provide the results of a nine month study assessing dissolved CH_4 levels in the raw influent of three large Australian wastewater treatment plants (WWTPs) fed by gravity sewers. Similar to recent international research and contrary to IPCC guidance, results show that gravity sewered wastewater contains moderate levels of CH_4 (≈1 mg L^{-1}). Dissolved CH_4 concentration correlated negatively with daily sewage flow rate (i.e. inversely proportional to sewer hydraulic residence time), with daily CH_4 mass loads on average some two-fold greater under low flow (dry weather) conditions. Along with sewage hydraulic residence time, sewer sediments are thought to interact with sewage flow rate and are considered to play a key role in gravity sewer CH_4 production. A per capita load of 78 g CH_4 person^{-1} y^{-1} is offered for gravity sewered wastewater entering WWTPs, with a corresponding emission estimate of up to 62 g CH_4 person^{-1} y^{-1}, assuming 80% water-to-air transfer of inflowing CH_4 in WWTPs with combined preliminary–primary plus secondary

treatment. Results here support the emerging consensus view that hydraulic operation (i.e. gravity versus pressurised, sewage flow rate) is a key factor in determining sewer CH_4 production, with gravity sewer segments likely to play a dominant role in total CH_4 production potential for large metropolitan sewer networks. Further work is warranted to assess the scale and temporal dynamics of CH_4 production in gravity sewers elsewhere, with more work needed to adequately capture and assess the scale of diffuse sewer network CH_4 emissions from sprawling urban settlements globally.

Keywords

Domestic and industrial wastewater; Greenhouse gas emissions; Methane; Municipal gravity sewers; Urban water sector

1. Introduction

With a carbon dioxide (CO_2)-equivalent 100-year global warming potential of 28 (non-climate–carbon feedback) and the second-largest radiative forcing after CO_2 (IPCC, 2013) methane (CH_4) is an important anthropogenic greenhouse gas (GHG). Present day anthropogenic CH_4 emissions equal or exceed those from natural sources and at around 1,800 ppb in 2011, global atmospheric CH_4 has increased 2.5-fold relative to pre-industrial levels. Despite a decade of near stability in global atmospheric CH_4 concentration during the 1990s, CH_4 levels are once again increasing (IPCC, 2013) and while total global CH_4 emissions are relatively well defined, the magnitude and dynamics of many individual CH_4 sources, including wastewater, remain poorly characterised (Dlugokencky *et al.*, 2011).

CH_4 is an unavoidable by-product of municipal wastewater collection and treatment, and occurs during anaerobic microbial metabolism of organic substrates. If not intentionally captured and flared, CH_4 emissions can occur from a range of processes including anaerobic reactors (digesters, lagoons, septic systems), overloaded aerobic systems, open sewers and receiving environments (Doorn *et al.*, 2006). Globally, the rate of CH_4 emissions from wastewater management practices has increased in recent decades as a result of an expanding and increasingly urbanised population (US EPA, 2006; Bogner *et al.*, 2007). In the year 2000, CH_4 emissions from global wastewater management were estimated to represent some 5–7% of the total anthropogenic CH_4 source (US EPA, 2006; Denman *et al.*, 2007); however, considerable uncertainties and gaps in emissions accounting methods remain (Doorn *et al.*, 2006).

While open sewers throughout the developing world are a long-accepted and likely significant source of CH_4 (Doorn and Liles, 1999; Doorn *et al.*, 2006), the extent to which enclosed municipal sewers in developed countries emit CH_4 has been much less clear. Current IPCC Guidelines for GHG inventories indicate that closed and underground sewers are "…not believed to be a significant source of CH_4" (Doorn *et al.*, 2006; p. 6.8). Contrastingly, other IPCC authors stated around the same time that "Substantial emissions of CH_4 and N_2O can occur during wastewater transport in closed sewers…" (Bogner *et al*. 2007; p. 589). Remarkably, no referenced basis was provided in support of either claim.

Despite the early recognition by Czepiel *et al*. (1993) of appreciable CH_4 generation in the "influent lines" of a domestic wastewater treatment plant (WWTP), there was little research

interest in sewer CH_4 during the ensuing 15 years. Since then it has emerged that underground sewers do emit significant amounts of CH_4 (Guisasola *et al.*, 2008; Foley *et al.*, 2009), with this limited work focusing on likely CH_4-producing 'hotspots' throughout sewer networks (i.e. anaerobic regions such as pressure mains, rising mains and pump station wet wells). In addition to these largely anaerobic zones, Foley *et al.* (2009) presented data from a limited field sampling campaign (1–2 days) which indicated that untreated domestic sewage exposed to the atmosphere was also methanogenic.

While this research provided evidence of CH_4 formation and anecdotal evidence of its persistence in gravity sewers, there remains a lack of information regarding the extent of CH_4 production and/or persistence in gravity sewer networks. Daelman *et al*. (2012), for example, stated that "…methane formation in sewer systems can be substantial, but actual quantities of methane entering a WWTP have as yet not been reported". At the same time, Willis *et al.* (2012), after detecting CH_4 emissions from a series of predominantly gravity-fed pumping stations, stressed that "…gravity sewer CH_4 emissions could be significant and warrant further research." Initial efforts to begin filling this gap were reported by Ren *et al*. (2013) who, following a four month study, reported relatively low levels of CH_4 in the raw influent of three Chinese WWTPs. Subsequent work has also reported on CH_4 emissions from sewer maintenance holes, pumping stations and sewer sediments (Chaosakul *et al.*, 2014; Liu *et al.*, 2014; Liu *et al.*, 2015a).

Accordingly, this research sought to provide new information on the levels and dynamics of CH_4 in gravity sewered wastewater and to better understand the contributing factors by correlating CH_4 data with key system parameters. The raw influent of three large, primarily domestic Australian metropolitan WWTPs was routinely sampled over a nine month period and analysed for dissolved CH_4 to estimate the extent of CH_4 production and/or persistence in gravity sewered wastewater. Such an extended investigation of raw sewage CH_4 levels does not exist in the literature and as such, new information is provided on the conveyance and temporal dynamics of this important GHG in gravity sewers.

2. Material and methods

2.1. Study sites and sampling protocol

Untreated wastewater was collected from the raw influent at three large WWTPs (Plants A, B and C) in the state of New South Wales, Australia during the period December 2011 to August 2012 (Australian summer–winter). These three WWTPs service a combined equivalent population of three million people; key details of the WWTPs, their catchments and influent sewage are provided in Table 1. All three WWTPs provide primary level treatment prior to offshore wastewater discharge to the adjacent continental shelf. Wastewater to all three WWTPs is of medium strength (Henze and Comeau, 2008) and mainly domestic in origin (≥70%), with Plant A receiving largely domestic wastewater, Plant B receiving ≈30% industrial wastewater and Plant C intermediary between Plants A and C. While there are some three hundred pumping stations throughout the sewer networks servicing the three WWTPs (Table 1), wastewater flow to each coastal plant is primarily by gravity. Detailed information on sewer gradients was unavailable from the managing water utility; however, literature data indicates that the lower reaches of the Plant B network are relatively flat (≈0.05%) (Henry, 1939), while the main trunk sewer supplying Plant C is steeper (1.2%) (Wang *et al*., 2012). The hydraulic residence time (HRT) of sewer networks supplying each WWTP varies considerably with incident weather conditions, but under dry weather flows is nominally 5 hours for Plant A, 21 hours for Plant B and 15 hours for Plant B.

During the nine month study, samples were collected on random weekdays a total of 11 times each for Plants A and B, with 12 sampling intervals for Plant C (see Short *et al*. (2014) and supplementary data Table S1 for more details). At each sampling interval, duplicate wastewater samples were drawn from the raw WWTP influent stream prior to any treatment interventions and as such represent final sewer network effluent. Bubble-free grab samples for dissolved CH_4 analysis were collected without headspace in 300 mL borosilicate glass bottles and hermetically-sealed with chlorobutyl/45 rubber septa-containing caps (Wheaton Science Products). Due care was taken to minimise the atmospheric exposure of sampled wastewater during sampling. Parallel grab samples (500 mL; Nalgene®) were also collected for conventional water quality analyses. To investigate possible sub-daily patterns in CH_4 dynamics, a limited one-off sampling programme was also carried out at Plant B in winter (dry weather flow conditions) during which the plant influent was sampled hourly from 0930–1430 (i.e. six times). Sewer headspace air samples (≈20 mL) were also periodically collected as close as practicable to the point of sewer entry to each WWTP using a gastight syringe (25 mL, Agilent) and stored overpressure in pre-evacuated Exetainer® vials (12 mL;

Labco Ltd.) until analysis. All wastewater samples were stored at ≤4°C during transit and extraction of dissolved CH_4 was always performed within 6 hours of sample collection.

2.2. Water quality analyses

2.2.1. Dissolved CH_4

Dissolved CH_4 was extracted from duplicate wastewater samples using a single-phase syringe-based static headspace protocol modified from Hemond and Duran (1989) and Hamilton and Ostrom (2007). Briefly, this protocol involved mixing equal volumes (25 mL) of wastewater and ultra-high-purity helium (>99.995%, BOC Australia) in a hermetically sealed 60 mL syringe under elevated temperature (40°C) until the point of CH_4 equilibration. 50% w/v $ZnCl_2$ solution was added to sample syringes (0.4% w/v final) to inhibit biological activity after Nicholls *et al.* (2007). Headspace-extracted gas samples (≈25 mL) were stored under positive pressure in pre-evacuated Exetainer® vials (12 mL; Labco Ltd.) until analysis. CH_4 analysis was performed by flame ionisation detection on an Agilent 7890A gas chromatograph (Agilent Technologies) fitted with a GS-CarbonPLOT capillary column (30 m × 0.32 mm ID × 3.0 μm film; Agilent Technologies) and using a splitless manual injection protocol (50 μl sample). Instrument operating conditions during CH_4 analyses were as follows: oven and inlet temperature 55°C isothermal; N_2 carrier gas (13.4 psi) 3 mL min^{-1}; N_2 makeup gas 27 mL min^{-1}; H_2 flow 40 mL min^{-1}; air flow 400 mL min^{-1}; detector temperature 250°C. CH_4 retention time under these conditions was <1.5 minutes.

Calibration of the GC–FID was performed using reference gas standards (CALGAZ; Air Liquide) bracketing the range of sample CH_4 concentrations encountered (10–1000 ppmv ±2% in air matrix). Analyte peak areas were integrated using ChemStation software (Agilent Technologies) and sample CH_4 concentrations were determined from mean peak areas of replicate sample chromatograms following GC–FID calibration. Measured CH_4 wet mole fractions in headspace-equilibrated gas samples were corrected for the partial pressure of water vapour and then used to calculate original wastewater sample CH_4 concentrations according to Henry's Law and published solubility coefficients (Rettich *et al.*, 1981).

2.2.2. Conventional wastewater parameters

Various wastewater data (i.e. daily flow rate, $cBOD_5$, COD, pH, temperature) were obtained from the managing utility's routine monitoring records. For other key parameters, wastewater samples were analysed. For dissolved nutrients, 50 mL aliquots were pre-filtered

189 (Whatman® GF/F; 0.7 μm) and frozen (−20°C) in HDPE containers until analysis.
190 Ammonia- (NH_4^+-N), nitrate- (NO_3^--N) and nitrite-nitrogen (NO_2^--N) were analysed via flow
191 injection analysis (Lachat Instruments, QuikChem®) using standard protocols. Total nitrogen
192 (TN) and total organic carbon (TOC) analyses of unfiltered samples were done using an
193 AnalytikJena multi N/C 2100S analyser. Dissolved oxygen (DO) was measured with a
194 Clark-type electrode (Thermo Scientific Orion 5-Star). Total suspended solids (TSS) was
195 determined according to standard protocols (Clesceri *et al.*, 1999).
196

Table 1. Wastewater treatment plant, sewer network and mean raw wastewater characteristics (± SD) for the three study sites during the 2011–2012 financial year (SWC, 2012). Unless otherwise specified, water quality data are given in units of mg L^{-1}.

WWTP	*Catchment area* (km^2)	*EP*[a] ($\times 10^6$)	Pump stations *per* km^2	*Nominal* sewer *HRT*[b] *(h)*	*ADWF*[c] (ML d^{-1})	*Flow*[d] (ML d^{-1})	*TN*	NH_4^+-*N*	*COD*[e]	$cBOD_5$[f]	*TSS*	*pH*	*Temp.* (°C)
A	≈40	0.30	0.77	5	≈115	133	48 ± 8	36 ± 6	523 ± 77	200 ± 27	231 ± 41	7.6 ± 0.3	23 ± 1.5
B	≈500	1.41	0.23	21	≈450	560	45 ± 11	30 ± 6	585 ± 148	254 ± 89	304 ± 85	7.1 ± 0.2	21 ± 2.2
C	≈420	1.20	0.20	15	≈350	444	47 ± 13	34 ± 9	570 ± 130	223 ± 68	262 ±109	7.1 ± 0.2	21 ± 1.8

[a] Equivalent population served

[b] Hydraulic residence time

[c] Long-term average dry weather flow rate

[d] Actual recorded average daily flow rate

[e] Chemical oxygen demand

[f] Carbonaceous five-day biochemical oxygen demand

205 *2.3. Wastewater CH_4 mass loads and emissions estimates*

206 With a Henry's Law constant of 0.0014 M/atm. at 25°C (Rettich *et al.*, 1981), the equilibrium
207 solubility concentration for CH_4 in water is extremely low (<0.05 μg L^{-1}) under ambient
208 atmospheric conditions (Dlugokencky *et al.*, 2011). Consequently, a strong driving force exists
209 for atmospheric ventilation (emission) of dissolved CH_4 from methane-supersaturated wastewater
210 streams. As such, all data presented here is given as 'excess' delta CH_4 (ΔCH_4) and represents
211 the mass of dissolved CH_4 above the normal 100% saturation concentration (i.e. maximum
212 potential CH_4 emission assuming 100% ΔCH_4 water-to-air mass transfer). Others have adopted
213 similar assumptions regarding the ultimate atmospheric ventilation of supersaturated wastewater
214 GHGs including CH_4 (Guisasola *et al.*, 2008; Foley and Lant, 2009; Foley *et al.*, 2009; Guo *et*
215 *al.*, 2012; Liu *et al.*, 2015a; Willis *et al.*, 2016) and the validity of this assumption is revisited in
216 the Results and Discussion. Calculated sewage CH_4 mass loads for the three study WWTPs (kg
217 CH_4 d^{-1}; t CH_4 y^{-1}) were also normalised to the equivalent population served by each plant to
218 derive per capita equivalent methane loads (g CH_4 $person^{-1}$ $year^{-1}$). These were then combined
219 with literature reports of air-to-water mass transfer efficiency during on-site wastewater treatment
220 processing (refer Section 3.5) to estimate per capita emission rates to allow for comparison with
221 CH_4 emission factors reported internationally.
222
223 *2.4. Data analyses*

224 Links between various wastewater parameters and CH_4 were explored via correlation analyses.
225 Differences among average wastewater parameter values between the three WWTPs were
226 identified by one-way analysis of variance (ANOVA). All statistical analyses were performed in
227 Prism® 6 (GraphPad Software Inc., CA) in line with underlying data normality assumptions.
228
229
230 **3. Results and Discussion**

231 *3.1. Wastewater characteristics*

232 Table 2 presents the key influent wastewater data for the three study WWTPs during the
233 combined nine month monitoring period. Although the sewers are configured to separate sewage
234 from stormwater, all WWTPs serve ageing gravity sewer networks (Hector, 2011) and as such,
235 considerable stormwater inflow and infiltration occurs during rainfall events. It is apparent in the
236 Table 2 daily flow data that the monitoring period encompassed several heavy rainfall events.
237 For example, for WWTPs A and B, recorded peak flows were some 45% and 80% greater than

238 respective long-term average dry weather flow rate (ADWF), with one high flow event for Plant
239 C more than 2.5-fold above the rated ADWF (compare Table 1 and 2). In the context of these
240 high peak flow events, it is noteworthy that the monitoring period encompassed very strong La
241 Niña conditions, during which record-breaking rainfall was recorded throughout much of
242 Australia including the study region; La Niña conditions concluded mid-way through the study
243 period in March 2012 (Bureau of Meteorology, 2012). These high peak wastewater flow rates,
244 particularly for the larger catchments of WWTPs B and C, reflect the strong stormwater
245 component of sewage flows under wet weather conditions and resulted in substantial dilution of
246 some wastewater quality parameters on these days (see Table 2 parameter minimums). Rainfall
247 dilution of wastewater constituents to this degree is common during storm events for combined
248 sewage (e.g., Nielsen et al., 1992).
249
250 Conventional wastewater parameters of Table 2 (i.e., COD, TN, NO_x^--N) across all three study
251 WWTPs were within the range of those commonly reported for untreated domestic wastewater
252 (e.g., Henze and Comeau, 2008; Ren *et al*., 2013). Positive relationships were evident between
253 daily flow and the levels of total oxidised nitrogen (i.e. NO_2^--N + NO_3^--N) in the influent
254 wastewater of all three WWTPs. The nature and likely origins of these relationships are
255 discussed in more detail elsewhere in the context of sewer nitrous oxide (N_2O) production (Short
256 *et al.*, 2014). Briefly, it is thought that under aerobic/hypoxic conditions, partial or complete
257 biological ammonia oxidation occurs in the gravity sewers of all WWTPs, with the yields of
258 product NO_x^--N increasing under high flow conditions. In the context of the current work, the
259 ubiquitous presence of NO_x^--N, at times in the order of 0.5–1.0 mg L^{-1}, suggests that wastewater
260 conditions in the gravity sewers supplying our study WWTPs were most likely oxidising.
261 Elsewhere, the levels of dissolved oxygen (DO) in Danish gravity sewered wastewater was
262 reported to be in the order of 1–4 mg L^{-1} (Nielsen *et al.*, 1992), with similar DO concentrations
263 (≈0.8–2.1 mg L^{-1}) seen in gravity sewers in Thailand (Chaosakul *et al*., 2014). Periodic
264 wastewater DO measurements here revealed concentrations of ≈0.5–3.5 mg O_2 L^{-1} (Table 2),
265 indicating that hypoxic to fully aerobic conditions persisted in the bulk wastewater. The
266 implications of this observation for sewer CH_4 dynamics are discussed further in Section 3.3.
267
268 *3.2. Dissolved wastewater CH_4*
269 Average levels of dissolved CH_4 in the raw influent were similar across the three surveyed
270 WWTPs during the nine month period (1-way ANOVA; $F_{(2,31)} = 2.89$; $p = 0.071$), ranging from

≈0.5 mg L^{-1} for plants A and C up to ≈0.8 mg L^{-1} for plant B (Table 2). Although just beyond the 5% limit of statistical significance, Plant B wastewater CH_4 levels were notionally higher than Plants A and C. This apparent difference could relate to the higher organic strength (COD) of the Plant B influent (Table 2) as well as the longer sewer network HRT (Table 1). Comparing Table 2 CH_4 data with that of other Australian work, levels were similar to those seen in a pressure main pump station wet well receiving fresh domestic sewage (i.e. 1.0–1.9 mg CH_4 L^{-1}; Foley *et al*., 2009). Law *et al.* (2012) also reported similar quantities of sewer-generated CH_4 (≈3.6 mg L^{-1}) in the raw influent of a small sub-tropical Australian WWTP following a three-day sampling program. Gravity sewage CH_4 levels here (Table 2) were on average some 10–20-fold lower than those reported for Australian pressure sewers (rising mains) elsewhere, with dissolved CH_4 concentrations there in the range of 5–30 mg/L (Guisasola *et al.*, 2008; Foley *et al.*, 2009; Liu *et al.*, 2015b).

Internationally, Daelman *et al*. (2012) provide data on raw sewage CH_4 mass flow rates through a Dutch WWTP, and based on their reported mean mass CH_4 flow data (9 kg CH_4 h^{-1}) and average wastewater flow rate (≈3 ML h^{-1}), raw sewage CH_4 concentrations were comparable to our data at around 3 mg L^{-1}. Recent Swedish research profiling dissolved CH_4 in gravity sewer mains (sewage temperature ≈14°C) produced very results similar to ours (0.06–0.6 mg L^{-1}), with this work also demonstrating that the rate of CH_4 generation in gravity sewers was a factor of 10 lower than in equivalent pressurised segments (Isgren and Mårtensson, 2013). This observation of 10-fold higher CH_4 generation rates in pressurised relative to gravity sewers fits well when comparing our gravity sewage data (≈0.6 mg CH_4 L^{-1}; Table 2) with the Australian rising main data of both Foley *et al.* (2009) (i.e. ≈5 mg CH_4 L^{-1}) and Liu *et al.* (2015b) (i.e. ≈9 mg CH_4 L^{-1}). Chaosakul *et al.* (2014) provide several days' of wastewater CH_4 data (3 hourly) from a 1 km long, 1 m diameter combined gravity sewer in Thailand (sewage temperature ≈33°C). Dissolved CH_4 levels there were on average some 10 to 20-fold higher than ours observed (Table 2) despite a substantially lower wastewater COD (≈180 mg L^{-1} during dry weather) and comparable HRT (28 h and 8 h under dry and wet weather respectively). Clearly the Thai sewage of Chaosakul *et al*. (2014) was much warmer than our Australian sewage (≈22°C) and the Swedish sewage of Isgren and Mårtensson (2013) (≈14°C) and given the recognised importance of temperature on methanogenesis (mesophilic optimum between 35–40°C), temperature probably played a determining role in the higher observed CH_4 levels. Accordingly, our CH_4 data should be interpreted within the appropriate climate context.

Elsewhere, Wang *et al.* (2011) reported much lower raw wastewater CH_4 levels (≈0.013 mg CH_4 L^{-1}) entering a northern Chinese WWTP than we observed. In the case of Wang *et al.* (2011), however, the raw sewage also contained some two- to five-fold lower COD levels (≈100–300 mg L^{-1}) than our wastewater (≈500–600 mg L^{-1}; Table 1). Following a four month investigation of three primarily domestic WWTPs in northern China, Ren *et al.* (2013) reported very low mean dissolved CH_4 levels in the raw influent of ≈4–9 μg L^{-1} across the three plants (influent CODs of between 140–1200 mg/L). These concentrations were up to several orders of magnitude below those encountered here (Table 2) and it is unclear why levels there were so low. According to Willis *et al*. (2016) sewer CH_4 production is practically independent of sewage COD at concentrations >100 mg L^{-1}, so organic strength may not be the primary driver for the low influent wastewater CH_4 levels encountered at these Chinese WWTPs. Most likely, different sewage temperature (as low as 12°C) and sewer configuration (e.g., proportion of combined vs. separate and pressurised vs. gravity segments, pipe diameter and sewage flow rate/HRT) played a determining role; however, neither of these studies provide any detail on the nature of the sewers supplying these WWTPs.

While we encountered dissolved CH_4 in raw wastewater at concentrations greatly exceeding that of normal atmospheric equilibrium solubility (<0.05 μg L^{-1}; Section 2.3), our end-of-pipe dataset does not allow us to be conclusive regarding its upstream origins (i.e. gravity vs. pressure sewer reaches). Recent work by Chaosakul *et al*. (2014) and Liu *et al.* (2015a; 2015c) has shown that gravity sewers are indeed substantially methanogenic as well as being an ineffective CH_4 sink. This suggests that our measured CH_4 is likely to have originated in both gravity and pressurised sewer segments (pump station rising mains); however, the relative contribution of each sewer type to the observed CH_4 is unknown.

Looking at the relative pump station density (i.e. number of pressure sewer mains) in each WWTP sewer network (Table 1), there was no statistically discernible association between this parameter and influent sewage CH_4 concentrations (Table 2) at each site. While details were not available on the various rising main dimensions and pump station operations across each sewer network for a full and proper comparison, it does suggest that pressure sewers may not be the dominant driver for sewer CH_4 production in these systems. Indeed, with sewer CH_4 production recognised as a surface area-dependent (areal) process in both rising mains (biofilms) and gravity

sewers (biofilms plus sediments) (Liu et al., 2015a; Liu *et al*., 2016), it is likely that for extensive sewer networks such as those here, gravity sewers contribute relatively more to total network CH_4 generation than pressure sewers, since their combined surface area will be orders of magnitude greater. For example, the sewer network of Plant C comprises some 3,650 km of sewer pipes and 84 major pumping stations (Wang *et al*., 2012). Assuming a nominal rising main length of 800 m, the equivalent length of pressure sewers is around 65 km, or <2% of the total linear piped network. If we then assume—as detailed above—that rising mains produce CH_4 at levels 10-fold greater than equivalent gravity sewers, the relative contribution of gravity sewers to total CH_4 production in this network will still be one order of magnitude greater.

3.2.1. Temporal variability in wastewater CH_4

While there was considerable temporal variability in wastewater CH_4 levels at each WWTP during the nine month study (daily CH_4 concentrations varied by some 20-fold; Table 2), average CH_4 levels were comparable between the three WWTPs. In light of recently emerging evidence showing significant (up to several-fold) diurnal variability in sewer CH_4 production elsewhere (Liu *et al.*, 2014; Liu *et al.*, 2015a; Liu *et al.*, 2015b), one limitation of our dataset is that any diurnal variation in wastewater CH_4 is not accounted for by our single-point daily grab sampling regime (sampling was done at 1000, 1200 and 1500 hrs for WWTPs C, A and B respectively). To address this gap, a one-off hourly grab sampling campaign was undertaken at plant B between 0930 and 1430 during dry weather flow conditions (see Section 2.1 for details). Results from this limited sub-daily monitoring campaign revealed little variation in dissolved CH_4 concentration (mean of 1.9 (±0.1) mg CH_4 L^{-1}). Instantaneous flow rates at each sampling interval obtained from the utility's online data system also showed relatively constant flow conditions during this five hour sampling period, increasing slightly from around 320 ML d^{-1} in the morning, to ≈400 ML d^{-1} at 1500 hrs. This relative stability in sewage flow may help explain the consistent wastewater CH_4 concentrations seen during this time, given the recognised importance of sewage flow rate (i.e. sewer HRT) on sewer CH_4 generation (see Section 3.3 for an analysis of CH_4 versus sewage flow rate).

Similarly to our one-off intensive sampling effort, Isgren and Mårtensson (2013) conducted an intensive one-day sampling program at the inlet of a Swedish WWTP (approx. hourly sampling between 0800–1700 hrs). Notably, this work also showed consistent wastewater CH_4 concentrations of between ≈0.4–0.7 mg CH_4 L^{-1}, with the highest levels encountered early in the

morning, something thought to have been related to the low sewage flow rates (i.e. longer sewage HRT) at that time of day. Depending on how well our routine sampling intervals for each WWTP reflected the true 24 hour average CH_4 profile, levels may be slightly higher or lower than the long-term daily average values reported in Table 2; although based on recent continuous monitoring work elsewhere (Liu *et al.*, 2014; Liu *et al.*, 2015a; Liu *et al.*, 2015b), it is likely that our data provide a reasonable 'order of magnitude' approximation of the true values. Overall and despite our three WWTPs having quite different sewer networks in terms of areal size, slope, nominal HRT and pump station density (Table 1) and despite the study encompassing a variety of weather and sewage flow conditions (Table 2), our long-term average wastewater CH_4 data were relatively consistent across all three WWTPs, suggesting that the data are reliable.

3.3. Relationships between CH_4 and other key parameters

The primary factor regulating CH_4 generation potential in wastewater is the amount of bio-available organics (i.e. COD or $cBOD_5$). Other key factors influencing sewer methanogenesis include temperature, HRT (sewage flow rate), pH and the presence of inhibitory substances including DO and various oxidised nitrogen species (Liu *et al.*, 2015a). We found no evidence of detectable relationships between CH_4 levels and wastewater temperature, pH or dissolved O_2; the absence of a detectable relationship between wastewater CH_4 and temperature in particular may relate to the temporal stability of this parameter (Table 1). Significant negative relationships were found between log-normal wastewater CH_4 concentrations and daily flow rate (Table 2) for WWTPs A (Pearson $r = -0.739$; $p = 0.009$), B ($r = -0.862$; $p = 0.0006$) and C ($r = -0.907$; $p < 0.0001$) (Figure 1), with this relationship possibly due to a more dilute (lower COD) sewage and shorter sewer HRT under high flow conditions, providing less favourable conditions for CH_4 generation. Previous work has shown that reduced sewage flow rates and longer sewer HRTs leads to increased CH_4 production (Guisasola *et al.*, 2008; Sun *et al.*, 2015). For our data, the negative flow versus wastewater CH_4 association of Figure 1 meant that under normal dry weather conditions and despite the lower daily sewage volumes, total daily ΔCH_4 mass load was on average much higher than under wet weather conditions (i.e. by some 1.4, 1.9 and 3.5-fold for plants A, B and C respectively). This finding may be of importance for water authorities in trying to understand their sewer CH_4 profile, in that both local climatic (Section 3.2) and weather conditions are likely to be key regulators of sewer CH_4 production. Additionally, it suggests that total CH_4 generation in combined sewers (stormwater + sewage) is likely to be less than in equivalent separate sewers serving the same population. The finding could also have

implications for the implementation of future sewer CH_4 abatement strategies, in that any future such efforts should target CH_4 abatement interventions under dry weather conditions in particular in order to maximise overall GHG mitigation returns.

Internationally, others have reported a similar negative 'flow versus CH_4' relationship in gravity sewers. For example, Chaosakul *et al*. (2014), reporting on wastewater CH_4 data from a Thai combined gravity sewer, showed that average CH_4 levels under dry weather conditions (10.1 mg L^{-1}; sewer HRT ≈28 h) were around two-fold higher than during wet weather conditions (4.6 mg L^{-1}; sewer HRT ≈8 h). Mean COD levels in their combined sewage were also three-fold higher under dry weather conditions (175 mg L^{-1}) compared to wet weather (59 mg L^{-1}), with the notably low organic strength of their sewage due to household septic tank/cesspool pre-treatment prior to sewer disposal.

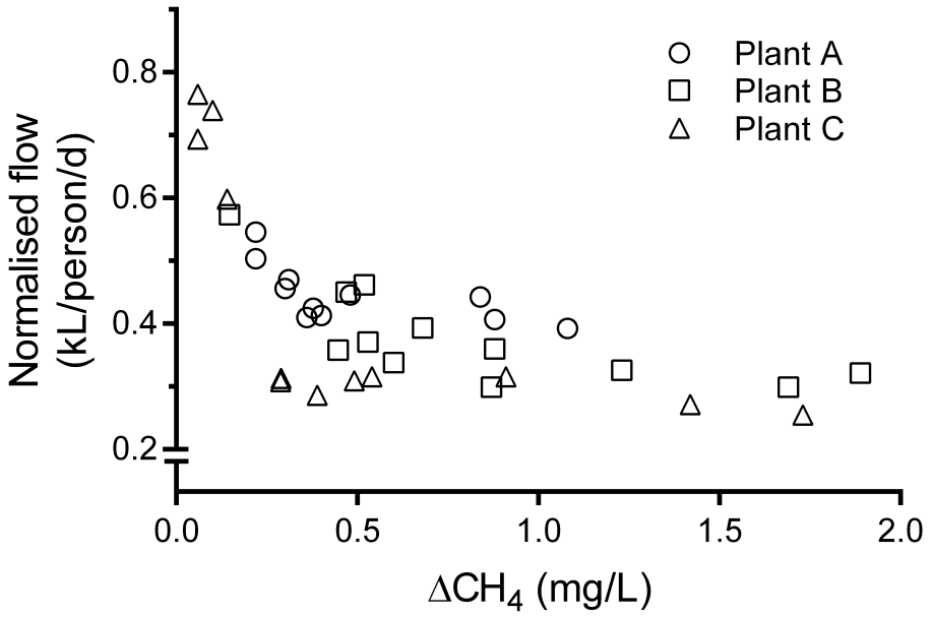


Figure 1. Scatter plot showing the negative association between daily wastewater flow rate (*y*-axis) and dissolved ΔCH_4 (*x*-axis) in the influent of each wastewater treatment plant.

Table 2. Summary of influent wastewater quality data for the three studied WWTPs during the December 2011 to August 2012 monitoring period. Mean values for each parameter given alongside corresponding data range (daily min; max). See Table S1 for full dataset.

WWTP	*Flow* ($ML\ d^{-1}$)	ΔCH_4 ($mg\ L^{-1}$)	*COD* ($mg\ L^{-1}$)	ΔN_2O[a] ($\mu g\ L^{-1}$)	*TN* ($mg\ L^{-1}$)	*C/N ratio* (COD/TN)	*DO*[b] ($mg\ L^{-1}$)	NO_x^--*N* ($mg\ L^{-1}$)
A	134 (118; 164)	0.50 (0.22; 1.1)	475 (432; 548)	7.4 (0.3; 42.1)	65 (51; 78)	7.5 (6.2; 10)	2.5 (0.8; 3.7)	0.07 (0.02; 0.26)
B	535 (421; 807)	0.83 (0.15; 1.9)	549 (459; 785)	9.8 (2.1; 48.9)	55 (20; 67)	11 (6.8; 28)	2.3 (0.6; 3.0)	0.07 (0.02; 0.43)
C	519 (307; 921)	0.53 (0.06; 1.7)	548 (439; 713)	7.7 (1.1; 42.5)	48 (18; 67)	13 (7.6; 30)	2.7 (2.2; 3.5)	0.23 (0.02; 1.22)

a Previously published data of Short *et al*. (2014)

b Dissolved oxygen

Contrasting the CH_4 data here with equivalent N_2O data for the same wastewater samples (Short *et al*., 2014), there was some evidence of negative correlations between log-normal raw wastewater CH_4 and N_2O concentrations at two of the three WWTPs (A, $r = -0.710$, $p = 0.014$; B $r = -0.597$, $p = 0.053$), with this negative relationship not statistically significant at plant C ($r = -0.407$, $p = 0.190$). Interestingly, once the sample size was increased by pooling the data from all three WWTPs and the correlation analysis rerun, the tenuous negative relationship between N_2O and CH_4 became statistically significant ($r = -0.365$; $p = 0.034$; $n = 34$). This finding is interesting and while the origins of CH_4 and N_2O are biologically distinct, it suggests that sewer conditions favourable for N_2O production are less favourable for CH_4 production and *vice versa* (see Short *et al*., 2014 for information on sewer N_2O production mechanisms), implying a likely pattern of alternating production for these two important GHGs. Contrasting this with equivalent paired raw wastewater N_2O and CH_4 data of Ren *et al*. (2013), a similar negative association is apparent; although in that case, not statistically significant ($r = -0.30$; $p = 0.430$).

Regarding the underlying mechanisms for this trend, sewer CH_4 production/consumption rate may vary with changing wastewater oxidation–reduction potential (ORP) linked to flow rates and stormwater influx which may also impact N_2O production (Short *et al*., 2014); others have reported on the negative association between wastewater ORP and dissolved CH_4 for example (Ren *et al.*, 2013). Aside from bulk ORP effects, there may be potential for direct inhibitory interactions from oxidised nitrogen species. For example, NO_3^-, NO_2^-, nitric oxide (NO) and N_2O are all inhibitory to methanogenesis at varying concentrations (Klüber and Conrad, 1998). While periods of high flow generally coincided with elevated levels of NO_3^- and NO_2^- (Short *et al*., 2014), there was no evidence here of significant negative relationships between these two parameters and CH_4, with peak concentrations of the more potent NO_2^- some 5–10-fold below those that would be substantially inhibitory (Klüber and Conrad, 1998). For N_2O and despite the apparent negative association between CH_4 and N_2O, this relationship is not considered causal, since peak N_2O concentrations (Table 2) were some 10 to 50-fold below inhibitory levels (Klüber and Conrad, 1998). Inhibition by other intermediates such as NO and free nitrous acid (the protonated form of NO_2^-) are also unlikely, with peak free nitrous acid levels in our wastewater (<0.001 mg HNO_2 L^{-1}) well below that which would inhibit methanogenesis (Jiang *et al.*, 2011).

Exploring further the possible mechanisms behind the negative flow versus CH_4 relationship of Figure 1, sewer sediment may play an important role. Liu *et al*. (2015c) demonstrated that under static laboratory conditions, gravity sewer sediments are substantially methanogenic, with CH_4 production rates similar to that of pressure sewer biofilms. Early work by Vollertsen and Hvitved-

Jacobsen (2000) in laboratory flumes also showed that for reconstituted gravity sewer sediments under simulated low flow conditions (0.2 m s^{-1}), sediment beds quickly became substantially methanogenic within 1–2 days, producing large (up to 2 ml) gas-filled cavities of up to 14% CH_4. With increasing incubation time (up to 4 days), these sediments became increasingly bulky, but less dense and more unstable due to the development of gas cavities, making them more prone to erosion under high flows (0.45 m s^{-1}). For combined sewers, significant erosion and mobilisation of sewer sediments is known to occur during storm events, in particular during the early onset of wet weather flows via the so-called 'first flush' phenomenon (Verbanck, 1990; Ashley *et al*., 1992). Interestingly, Daelman *et al*. (2012) showed that such first flush events also correlate with peak wastewater CH_4 emissions from wastewater treatment basins (approx. 10-fold above dry weather baseline), most likely due to disturbance of sediment-associated CH_4 in upstream sewers as described above. Sediments washed away during high flow storm events then take several days (or longer) to restore (Verbanck, 1990), suppressing sewer methanogenic potential for some time following a return to normal dry weather flows—something evident in the data of Daelman *et al*. (2012). In the context of our results, it is likely that during storm events (see Section 3.1), accumulated sewer sediments were disturbed and eroded such that under high flow conditions, methanogenic potential was diminished. This idea was supported in principle by the positive correlation between daily flow rate and daily mass TSS load (t/d; Table S1) for the pooled three-plant dataset ($r = 0.627$; $p < 0.0001$; $n = 33$), such that total daily sewage solids loads were significantly higher under high flow conditions due to sediment mobilisation.

3.4. Sewer headspace CH_4

The concentration of CH_4 in the sewer headspace gas sampled from point of entry to the WWTPs ranged from just several times (≈5 ppmv) that of the ambient atmosphere (≈1.8 ppmv; Dlugokencky *et al*., 2011) to some 260 ppmv, with an average of ≈45 ppmv (see Table S1 for complete dataset). Although the sampling of headspace gas in the sewer outlet was performed only intermittently, higher headspace CH_4 levels did appear to coincide with periods of reduced daily wastewater flow rates as observed for dissolved CH_4 above. While our sewer headspace data were too sparse to draw firm conclusions, the results confirm that CH_4 was present in sewer headspace on average at concentrations greatly exceeding ambient levels. It also indicates that calculations of sewer CH_4 emissions here based solely on excess dissolved CH_4 at the WWTP inlet are conservative, since additional CH_4 losses would be expected to occur throughout the upstream sewer networks from open structures such as access holes, vents and gas relief valves for pressurised segments (see Section 3.5 of Short *et al*. (2014) for a more in-depth discussion).

While our survey encountered sewer headspace CH_4 levels several times higher than atmospheric, it is worth noting that considerably higher concentrations of CH_4 in sewer gas have been reported elsewhere (e.g., ≈1% and ≈2% for subtropical Australian gravity and pressure sewer gas respectively (Liu *et al.*, 2014); ≈1.2% in a rural Thai gravity sewer (Chaosakul *et al.*, 2014); and ≥5% in some US locations (Liu *et al.*, 2015a)). It should be emphasised that for our sewer headspace data, we consider them to underestimate true sewer headspace CH_4 levels, since access to the primary point of sewer entry at each WWTP was restricted, such that the air we sampled was almost certainly already heavily diluted by forced underground ventilation airflow before collection.

3.5. CH_4 mass loads and presumptive emissions for gravity sewered wastewater entering WWTPs

Equivalent total CH_4 mass loads and per capita normalised loads for the three WWTPs are shown in Table 3. Presumptive per capita CH_4 emissions are also offered in Table 3 for preliminary–primary only and combined preliminary–primary plus secondary treatment, based on a range of reported CH_4 stripping rates during wastewater processing (Wang *et al*., 2011; Daelman *et al*., 2012). While some research has highlighted the potential for significant (≈80%) biological oxidation of sewer-derived CH_4 during aerated secondary treatment processes (Daelman *et al.*, 2012), the assumption that the vast majority of dissolved CH_4 delivered to the inlet works of a WWTP ultimately reaches the atmosphere is commonly adopted (Guisasola *et al.*, 2008; Foley and Lant, 2009; Foley *et al.*, 2009; Guo *et al.*, 2012; Liu *et al.*, 2015a; Willis *et al*., 2016) and is supported by field observations. For example, work on the Dutch Papendrecht and Kortenoord WWTPs showed that nearly 50% of total plant-wide CH_4 emissions occurred during inlet works processing, with a further ≈33% of the residual CH_4 stripped from downstream aeration basins (i.e. ≥80% total flux of inflowing sewage CH_4 for preliminary–primary plus secondary treatment) (Foley *et al*., 2015). Wang *et al*. (2011) reported a very similar fraction of CH_4 flux during inlet works processing and preliminary treatment, with some 50–60% of inflowing CH_4 lost via inlet pumping and aerated grit chambers. In reality, the extent to which sewer-generated CH_4 ultimately reaches the atmosphere will vary according to WWTP process configuration (e.g., inlet works pump type, aerated versus non-aerated preliminary treatment), so our Table 3 emissions estimates should be interpreted within the recommended order of magnitude context.

Although our emissions estimates are based on dissolved CH_4 data and literature assumptions of effective water-to-air transfer, and are therefore not true 'emission factors', it is useful to contrast these values with CH_4 emission factors reported from WWTPs elsewhere. Czepiel *et al*. (1993) gave comparable emission factors of 16 g CH_4 person^{-1} y^{-1} from primary treatment processing (aerated grit tanks) and 39 g CH_4 person^{-1} y^{-1} for combined primary plus secondary treatment at a

very small (4 ML d^{-1}) WWTP, with this CH_4 assumed to have originated in the sewer network. Wang *et al*. (2011) provided emission factors for a large (300 ML d^{-1}) Chinese WWTP of ≈9–15 g CH_4 $person^{-1}$ y^{-1} (mean of 11.3 g CH_4 $person^{-1}$ y^{-1}) encapsulating both liquid and solids line treatment processes; although the vast majority of emitted CH_4 originated from wastewater line processes. Possible reasons for the divergence in our CH_4 data relative to that of Wang *et al*. (2011) were discussed in Section 3.2.

Daelman *et al*. (2012) following work on the Dutch Kralingseveer WWTP treating low strength (340 mg COD L^{-1}) domestic wastewater gave an emission factor of 22 g CH_4 $person^{-1}$ y^{-1} from plant headworks processing only. Based on uncertainties in the authors' own analysis, sewer-derived CH_4 emissions could feasibly be in the order of 45 g CH_4 $person^{-1}$ y^{-1}, or 15% of the quoted plant-wide emission factor of 306 g CH_4 $person^{-1}$ y^{-1}. Sewer-derived CH_4 emissions for two other Dutch WWTPs (i.e. Papendrecht and Kortenoord) were somewhat higher than our Table 3 estimates at ≈230g and 108 g CH_4 $person^{-1}$ y^{-1} respectively, based on 86% and 77% of the total respective plant-wide CH_4 emissions being able to be traced back to the influent sewage (Daelman *et al.*, 2012). Much like our own end-of-pipe estimates, the emission factors of Daelman *et al*. (2012) and those of other studies cited above are probably conservative of total sewer-derived CH_4 emissions, since they all exclude diffuse emissions originating from the upstream sewer network. Accordingly, we recommend that these values be interpreted within an order of magnitude context regarding probable system-wide sewer emissions and echo the recommendation of Foley *et al*. (2015) that further research is needed to characterise liquid-to-gas mass transfer processes for CH_4 in sewers.

553 **Table 3.** Flow-weighted annual average total and population-normalised CH_4 mass loads for
554 gravity sewered wastewater entering three WWTPs, alongside estimated annual per capita CH_4
555 emissions for preliminary–primary only and equivalent preliminary–primary plus secondary
556 wastewater treatment. Mean parameter values for each site are given alongside observed data range
557 (min; max) (see Table S1 for complete dataset).
558

WWTP	*ΔCH_4 mass load ($t\ CH_4\ y^{-1}$)*	*Per capita ΔCH_4 load ($g\ CH_4\ person^{-1}\ y^{-1}$)*	*Preliminary–primary only flux[a] ($g\ CH_4\ person^{-1}\ y^{-1}$)*	*Preliminary–primary + secondary flux[a,b] ($g\ CH_4\ person^{-1}\ y^{-1}$)*
A	23.4 (12.1; 46.4)	78.2 (40.4; 155)	39.1 (20.2; 77.5)	62.6 (32.3; 124)
B	148 (43.4; 313)	94.4 (30.8; 222)	47.2 (15.4; 111)	75.5 (24.6; 178)
C	72.2 (18.3; 194)	59.8 (15.3; 161)	29.9 (7.65; 80.5)	47.8 (12.2; 129)
Arithmetic mean	n/a	77.5	38.8	62.0
Population-weighted mean	n/a	78.4	39.2	62.7

559 [a] Assuming 50% of inflowing wastewater ΔCH_4 load is transferred to atmosphere during
560 preliminary–primary treatment based on data of Wang *et al*. (2011) and Daelman *et al*. (2012).
561 [b] Assuming a further 30% of inflowing wastewater ΔCH_4 load is transferred to atmosphere during
562 secondary treatment (Daelman *et al*., 2012). NB. Emissions estimates for combined
563 preliminary–primary plus secondary treatment are indicative only, since our WWTPs do not
564 have secondary treatment.
565
566
567 *3.6. Implications of sewer CH_4 for the international water sector*
568 Current international guidelines for estimating wastewater CH_4 emissions do not incorporate an
569 approach for estimating that from sewers. With year 2000 estimates of global population sewerage
570 rates starting at ≈30% (Van Drecht *et al.*, 2009), or some 1.8 billion people, this translates to annual
571 year 2000 sewer CH_4 emissions in the order of 2–4 Mt CO_2-e based on our average per capita
572 emission estimates (Table 3) and assuming a 100-year CH_4 global warming potential of 28. Using
573 equivalent Table 3 data minimum and maximums, global sewer CH_4 emissions could feasibly be
574 between ≈1–10 Mt CO_2-e; although we stress again that such estimates based on our end-of-pipe
575 sewage CH_4 data and literature-informed emissions estimates are most likely conservative and so
576 actual emissions could be higher still.
577

The above global sewer emissions estimate and associated uncertainty is significant for a range of activities in the water sector and beyond. For example, while present day sewer CH_4 probably constitutes a minor fraction (≤10%) of overall per capita wastewater CH_4 emissions for developed nations, the relative contribution of sewers to global wastewater CH_4 production is likely to increase in future in line with increased rates of population sewerage from improved sanitation (WHO/UNICEF, 2012), combined with increasing efforts by the water sector to capture scope 1 CH_4 (biogas) emissions from anaerobic processes for energy recovery as part of the sector's push toward energy- and carbon-neutrality (Hao *et al.*, 2015). Well-intentioned measures such as improved customer water use efficiency (voluntary or imposed) may also inadvertently increase sewer CH_4 emissions (e.g., Sun *et al.*, 2015), such that industry should be aware of these broader effects during policy setting or when conducting environmental life cycle assessments of their operations.

There are also broader potential consequences for sewer CH_4 in the international policy arena, with CH_4 a reportable GHG under the Kyoto Protocol (United Nations, 1998) and annual reporting of national wastewater CH_4 emissions required by Kyoto signatories in line with IPCC Guidelines (Doorn *et al.*, 2006). In the absence of good quality direct emissions data, such reporting is done according to generalised Tier 1 methodologies based on a default emission factor and national activity data. More accurate sectoral and national-level GHG emissions inventories will help industry in Annex I countries better understand their emissions and associated economic liabilities under relevant national carbon emissions pricing policy. Better-defined GHG sources such wastewater CH_4 should also improve the resolution of 'bottom-up' global CH_4 budgets (Dlugokencky *et al.*, 2011), helping to constrain international emissions accounting efforts which ultimately helps reduce the volatility of global carbon markets and boost investment in much-needed emissions reduction activities (Weiss and Prinn, 2011).

Regarding potential industry control strategies, there are several which may be suitable for reducing the future environmental impacts of sewer CH_4 emissions. Chemical dosing approaches primarily aimed at mitigating sulfide production and sewer corrosion (e.g., ferric salts, nitrate/nitrite, hydroxide for pH elevation and free nitrous acid) may provide auxiliary benefits in terms of methanogen inhibition (Liu *et al.*, 2015a); although in the case of nitrate/nitrite, the potential for inadvertent N_2O production must also be considered (Jiang *et al.*, 2011). To be effective, these chemicals will need to be dosed either continuously or at regular intervals and so their efficacy in the short-term will depend on the cost–benefit analysis of these chemicals, including capital savings from reduced sewer corrosion. In the longer-term and assuming that relevant GHG emissions

pricing policy is ultimately instated, future GHG emissions liability savings from avoided sewer CH_4 may help subsidise the cost of these chemicals. End-of-pipe solutions, such as composting air biofilters, also deserve further evaluation (Lebrero *et al.*, 2016) and may present opportunities for cost-effective CH_4 abatement under relevant future (inter)national GHG policies. Since CH_4 has a relatively short lifetime (≈9 years) and its atmospheric dynamics are close to steady state, CH_4 emissions mitigation efforts implemented today will quickly translate to real climate benefits (Dlugokencky *et al.*, 2011) and importantly, are also likely to be more cost-effective per tonne of abated CO_2-equivalents than comparable CO_2-based mitigation efforts (Winiwarter and Klimont, 2011; Short *et al.*, 2013).

4. Conclusions and recommendations

Until recently, CH_4 production from gravity sewers has been largely overlooked under the assumption that it is primarily an anaerobic (pressure) sewer process. Data here demonstrates that (aerobic/hypoxic) gravity sewers convey wastewater with moderate levels of CH_4 (≈1 mg L^{-1}), which translates to significant annual mass CH_4 loads in the order of a combined 250 t/y (≈7 kt CO_2-e/y) across the three study WWTPs. A strong negative relationship was observed between raw wastewater CH_4 concentration and daily sewage flow rate across the three WWTPs, with this association supported by recent research elsewhere and thought to relate to a reduced sewage HRT (shorter sewer contact time) under high flow conditions, as well as the disruption and mobilisation of methanogenic sewer sediments. This observation may have important implications for the conduct of industry intervention strategies seeking to mitigate sewer CH_4 production for GHG abatement purposes, with such interventions likely to have the greatest mitigation potential under dry weather conditions. A per capita wastewater load of 78 g CH_4 $person^{-1}$ y^{-1} was offered in the context of gravity sewered wastewater entering WWTPs. Corresponding per capita emission estimates (not emission factors) of 39 and 62 g CH_4 $person^{-1}$ y^{-1} were also presented for preliminary–primary treatment only and preliminary–primary plus secondary treatment respectively based on literature-reported water-to-air flux rates for inflowing sewage CH_4 during wastewater treatment. We acknowledge the limitations of our end-of-pipe data in trying to infer overall system-wide sewer CH_4 production and subsequent emissions, but suggest that these values—alongside those already in the literature—present useful 'order of magnitude' estimates for water utilities to begin understanding CH_4 emission potential from gravity sewage elsewhere.

While information on gravity sewer CH_4 production is starting to emerge, further research is warranted to better understand CH_4 production and emission in these systems (e.g., gravity sewer

mains of varying configuration and under different flow, and ventilation regimes). Work is also needed to characterise the liquid-to-gas mass transfer coefficient for CH_4 in gravity sewers in order to adequately model and predict diffuse emissions from sprawling sewer networks that are otherwise impractical to characterise via direct measurement. Such models should account for network pumping cycle effects on the introduction of outside air and headspace ventilation, as this will influence sewage–air flux processes and headspace exchange rates, both of which will affect overall CH_4 emission rates. Work to assess the scale of CH_4 emissions during the early onset of high flow (storm) conditions is also warranted, given the reported evidence of 'first flush' peaks in both wastewater CH_4 and suspended solids due to the mobilisation of methanogenic sewer sediments. In the absence of suitable and cost-effective in-sewer control through chemical dosing, there is scope for more research on engineered 'end-of-pipe' CH_4 abatement solutions such as methanotrophic air biofilters, as these may, under the right policy settings, present viable options for future GHG emissions abatement, particularly at likely CH_4 hotspots such as rising main gas relief points, headspace ventilation points along heavily loaded/long HRT gravity sewers, or aerated treatment processes at WWTPs.

Acknowledgments

This work was funded by the Australian Research Council (project DP1095722) and The University of New South Wales Faculty of Engineering Faculty Research Grants Program (project PS 27457). The primary author acknowledges financial support from the CRC for Low Carbon Living Ltd. (project RP2017) whose activities are supported by the Cooperative Research Centres program, an Australian Government initiative. Staff from the managing water authority are thanked for facilitating site access during field sampling and for data provision. Several anonymous reviewers are also thanked for their considered feedback which greatly improved the final manuscript.

References

Ashley RM, Wotherspoon DJJ, Coghlan BP,McGregor I. The Erosion and Movement of Sediments and Associated Pollutants in Combined Sewers. *Water Science and Technology* 1992;25(8):101–114.

Bogner J, Ahmed MA, Diaz C, Faaij A, Gao Q, Hashimoto S, Mareckova K, Pipatti R, Zhang T. Waste Management, in *Climate Change 2007: Mitigation. Contribution of Working Group III to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*. Metz B, Davidson OR, Bosch PR, Dave R, Meyer LA (eds), Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA; 2007.

Bureau of Meteorology. Record-breaking La Niña events: An analysis of the La Niña life cycle and the impacts and significance of the 2010–11 and 2011–12 La Niña events in Australia, Published by the Australian Government Bureau of Meteorology. ISBN: 978 0 642 70621 8; 2012.

Chaosakul T, Koottatep T, Polprasert C. A model for methane production in sewers. *Journal of Environmental Science and Health, Part A* 2014;49(11):1316–1321.

Clesceri LS, Greenberg AE, Eaton AD. (eds) Standard methods for the examination of water and wastewater. 20th Edition, American Public Health Association, American Water Works Association and the Water Environment Federation, Washington, DC; 1999.

Czepiel PM, Crill PM,Harriss RC. Methane emissions from municipal wastewater treatment processes. *Environmental Science & Technology* 1993;27(12):2472–2477.

Daelman MRJ, van Voorthuizen EM, van Dongen UGJM, Volcke EIP, van Loosdrecht MCM. Methane emission during municipal wastewater treatment. *Water Research* 2012;46(11):3657–3670.

Denman KL, Brasseur G, Chidthaisong A, Ciais P, Cox PM, Dickinson RE, Hauglustaine D, Heinze C, Holland E, Jacob D, Lohmann U, Ramachandran S, da Silva Dias PL, Wofsy SC, Zhang X. Couplings Between Changes in the Climate System and Biogeochemistry. In *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*. Solomon S, Qin D, Manning M, Chen Z, Marquis M, Averyt KB, Tignor M,Miller HL (eds), Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA; 2007.

Dlugokencky EJ, Nisbet EG, Fisher R, Lowry D. Global atmospheric methane: budget, changes and dangers. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences* 2011;369(1943):2058–2072.

Doorn MRJ, Liles D. Quantification of methane emissions and discussion of nitrous oxide, and ammonia emissions from septic tanks, latrines, and stagnant, open sewers in the world, U.S. EPA, National Risk Management Research Laboratory, Research Triangle Park, NC. EPA-600/R-99-089; 1999.

Doorn MRJ, Towprayoon S, Vieira SMM, Irving W, Palmer C, Pipatti R, Wang C. Chapter 6: Wastewater Treatment and Discharge. Eggleston HS, Buendia L, Miwa K, Ngara T, Tanabe K (eds), The National Greenhouse Gas Inventories Programme, The Intergovernmental Panel on Climate Change, Hayama, Kanagawa, Japan. ISBN 4-88788-032-4; 2006.

Foley J, Lant P. Direct methane and nitrous oxide emissions from full-scale wastewater treatment systems, WSAA Occasional Paper No. 24, Water Services Association of Australia. ISBN: 1 920760 47 4; 2009.

Foley J, Yuan Z, Keller J, Senante E, Chandran K, Willis J, Shah A, van Loosdrecht M, van Voorthuizen E. N_2O and CH_4 Emission from Wastewater Collection and Treatment Systems: State of the Science Report and Technical Report, GWRC Report Series, IWA Publishing, London, UK. ISBN: 9781780407340; 2015

Foley J, Yuan Z, Lant P. Dissolved methane in rising main sewer systems: field measurements and simple model development for estimating greenhouse gas emissions. *Water Science & Technology* 2009;60(11):2963–2971.

Guisasola A, de Haas D, Keller J,Yuan Z. Methane formation in sewer systems. *Water Research* 2008;42(6–7):1421–1430.
Guo L, Porro J, Sharma KR, Amerlinck Y, Benedetti L, Nopens I, Shaw A, Van Hulle SWH, Yuan Z, Vanrolleghem PA. Towards a benchmarking tool for minimizing wastewater utility greenhouse gas footprints. *Water Science and Technology* 2012;66(11):2483–2495.
Hamilton SK, Ostrom NE. Measurement of the stable isotope ratio of dissolved N_2 in ^{15}N tracer experiments. *Limnology and Oceanography: Methods* 2007;5:233–240.
Hao X, Batstone D, Guest JS. Carbon neutrality: An ultimate goal towards sustainable wastewater treatment plants. *Water Research* 2015;87:413–415.
Hector D. Sydney's Water Sewerage and Drainage System. *Journal & Proceedings of the Royal Society of New South Wales* 2011;144:3–25.
Hemond HF, Duran AP. Fluxes of N_2O at the sediment-water and water-atmosphere boundaries of a nitrogen-rich river. *Water Resources Research* 1989;25(5):839–846.
Henry FJJ (1939) The Water Supply and Sewerage of Sydney. Metropolitan Water Sewerage and Drainage Board, Sydney. Halstead Press, Sydney.
Henze M, Comeau Y. Wastewater Characterization, In *Biological Wastewater Treatment: Principles, Modelling and Design*. Henze M, van Loosdrecht MCM, Ekama GA, Brdjanovic D (eds), IWA Publishing. ISBN: 9781843391883; 2008. p. 33–52.
IPCC (2013) *Climate Change 2013: The Physical Science Basis, Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change*. Stocker TF, D Qin, G-K Plattner, M Tignor, SK Allen, J Boschung, A Nauels, Y Xia, V Bex, PM Midgley (eds.) Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.
Isgren M, Mårtensson P. Methane formation in sewer systems. MSc Thesis, Lund University, Sweden; 2013.
Jiang G, Gutierrez O, Sharma KR, Keller J, Yuan Z. Optimization of intermittent, simultaneous dosage of nitrite and hydrochloric acid to control sulfide and methane productions in sewers. *Water Research* 2011;45(18):6163–6172.
Klüber HD, Conrad R. Effects of nitrate, nitrite, NO and N_2O on methanogenesis and other redox processes in anoxic rice field soil. *FEMS Microbiology Ecology* 1998;25(3):301–318.
Law Y, Ye L, Ni B-J, Byers C, de Joong K, Lant P, Yuan, Z. Full scale monitoring of fugitive nitrous oxide and methane emissions from a wastewater treatment plant in Australia. Ozwater '12, Australian Water Association, 8th–10th May, Sydney Convention & Exhibition Centre, Sydney, Australia; 2012.
Lebrero R, López JC, Lehtinen I, Pérez R, Quijano G, Muñoz R. Exploring the potential of fungi for methane abatement: Performance evaluation of a fungal-bacterial biofilter. *Chemosphere* 2016;144:97-106.
Liu Y, Sharma KR, Murthy S, Johnson I, Evans T, Yuan Z. On-line monitoring of methane in sewer air. *Sci. Rep.* 2014;4:6637.
Liu Y, Ni B-J, Sharma KR, Yuan Z. Methane emission from sewers. *Science of the Total Environment* 2015a;524–525:40–51.
Liu Y, Sharma KR, Fluggen M, O'Halloran K, Murthy S, Yuan Z. Online dissolved methane and total dissolved sulfide measurement in sewers. *Water Research* 2015b;68:109–118.
Liu Y, Ni B-J, Ganigué R, Werner U, Sharma KR,Yuan Z. Sulfide and methane production in sewer sediments. *Water Research* 2015c;70: 350–359.
Liu Y, Tugtas AE, Sharma KR, Ni B-J,Yuan Z. Sulfide and methane production in sewer sediments: Field survey and model evaluation. *Water Research* 2016;89:142–150.
Nicholls JC, Davies CA, Trimmer M. High-resolution profiles and nitrogen isotope tracing reveal a dominant source of nitrous oxide and multiple pathways of nitrogen gas formation in the central Arabian. *Limnology and Oceanography* 2007;52(1):156–168.
Nielsen PH, Raunkjær K, Norsker NH, Jensen NA, Hvitved-Jacobsen T. Transformation of wastewater in sewer systems – a review. *Water Science & Technology* 1992;25(6):17–31.

Ren YG, Wang JH, Li HF, Zhang J, Qi PY, Hu Z. Nitrous oxide and methane emissions from different treatment processes in full-scale municipal wastewater treatment plants. *Environmental Technology* 2013;34(21):2917–2927.

Rettich TR, Handa YP, Battino R, Wilhelm E. Solubility of gases in liquids. 13. High-precision determination of Henry's constants for methane and ethane in liquid water at 275 to 328 K. *The Journal of Physical Chemistry* 1981;85(22):3230–3237.

Short MD, Daikeler A, Peters GM, Mann K, Ashbolt NJ, Stuetz RM, Peirson WL. Municipal gravity sewers: An unrecognised source of nitrous oxide. *Science of the Total Environment* 2014;468–469:211–218.

Short MD, Peters GM, Peirson WL, Ashbolt NJ. Marine nitrous oxide emissions: An unknown liability for the international water sector. *Environmental Science & Policy* 2013;33:209–221.

Sun J, Hu S, Sharma KR, Bustamante H, Yuan Z. Impact of reduced water consumption on sulfide and methane production in rising main sewers. *Journal of Environmental Management* 2015;154:307–315.

SWC (Sydney Water Corporation). Sewage Treatment System Impact Monitoring Program: Annual Data Report 2011–12, Sydney Water, Parramatta, NSW Australia; 2012.

United Nations. Kyoto Protocol to the United Nations Framework Convention on Climate Change; 1998. Available at: http://unfccc.int/key_documents/kyoto_protocol/items/6445.php (accessed 11/12/2015).

US EPA. Global Anthropogenic Non-CO_2 Greenhouse Gas Emissions: 1990–2020, Office of Atmospheric Programs Climate Change Division, U.S. Environmental Protection Agency, Washington, DC; 2006.

Verbanck M. Sewer sediment and its relation with the quality characteristics of combined sewer flows. *Water Science & Technology* 1990;22(10-11): 247–257.

Wang J, Zhang J, Xie H, Qi P, Ren Y, Hu Z. Methane emissions from a full-scale A/A/O wastewater treatment plant. *Bioresource Technology* 2011;102(9):5479–5485.

Wang YC, Nobi N, Nguyen T,Vorreiter L. A dynamic ventilation model for gravity sewer networks. *Water Science & Technology* 2012;65(1):60–68.

Weiss RF, Prinn RG. Quantifying greenhouse-gas emissions from atmospheric measurements: a critical reality check for climate legislation. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences* 2011;369(1943):1925–1942.

Willis J, DeClippeleir H, Graf W, Kumar A, Murthy S, Peot C, Regmi P, Satyadev A, Sharma K, Tanner H, Yuan Z. DC Water's Sewer-Methane Carbon Footprint, In: Proceedings of the Water Environment Federation, WEFTEC® 2016, Water Environment Federation; pp: 5836–5849; 2016.

Willis J, Shah A, Yuan Z, Sharma K, Joiner M, Bocarro R. Methane Evolution from Wastewater Conveyance, Water Environment Research Foundation and IWA Publishing. ISBN: 9781780404691; 2012.

Winiwarter W, Klimont Z. The role of N-gases (N_2O, NO_x, NH_3) in cost-effective strategies to reduce greenhouse gas emissions and air pollution in Europe. *Current Opinion in Environmental Sustainability* 2011;3(5):438–445.

World Health Organization/United Nations Children's Fund (WHO/UNICEF). Progress on Drinking Water and Sanitation: 2012 Update, WHO/UNICEF Joint Monitoring Programme for Water Supply and Sanitation. ISBN: 978-924-1503297; 2012.