

A literature-based comparison of embodied GHG emissions of forced main sewer additives with potential reductions in methane generation

Wayne J. Parker ^{a,*} and J. R. Walton^b

^a Department of Civil and Environmental Engineering, University of Waterloo, Waterloo, ON N2L 3G1, Canada

^b USP Technologies, 5640 Cox Rd., Glen Allen, VA 23060, USA

*Corresponding author. E-mail: wjparker@uwaterloo.ca

ABSTRACT

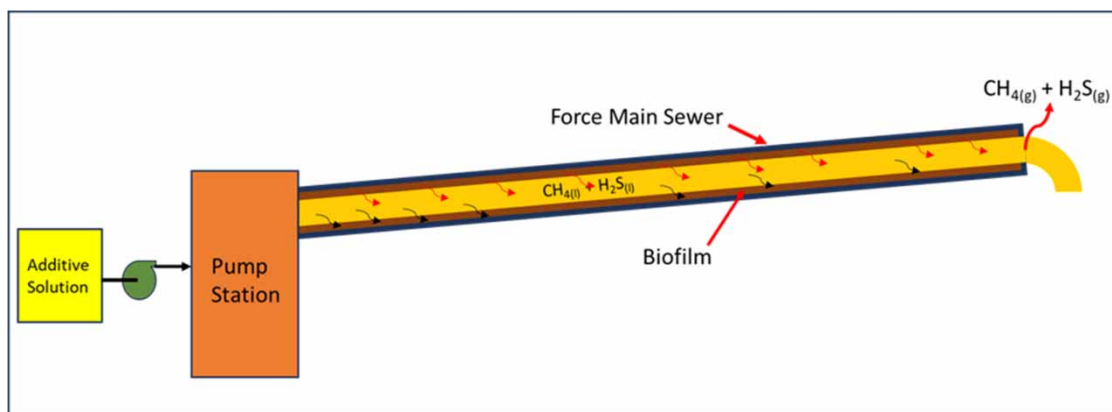
Fugitive emissions of methane (CH_4) from force main sewers are of increasing concern. Dosing of additives into force main sewers could be employed to mitigate methane emissions. However, all additives will have embodied greenhouse gas (GHG) emissions. This study examined commonly employed additives in terms of modes of action and potential to mitigate methane generation. Typical dosing strategies reported in the literature for each chemical were compiled and their embodied GHG emissions were summarised from sources in the literature. The net emissions considering mitigated methane generation and embodied GHG emissions were calculated on the basis of typical usage reported in the literature. The results revealed that biofilm shocking strategies and addition of iron have the greatest net reduction in GHG emissions. There is, however, uncertainty associated with the mechanisms by which iron reduces CH_4 generation in force mains. Furthermore, future changes in the sourcing of iron may increase its embodied emissions. A qualitative assessment of the impacts of additive use on downstream GHG emissions revealed that they are highly case specific.

Key words: embodied emissions, greenhouse gases, methane, mitigation, sewer, wastewater

HIGHLIGHTS

- Sewer additives for reducing CH_4 generation are compared.
- Embodied emissions of additives are estimated.
- Estimates of embodied emissions with reductions in CH_4 generation are compared.
- Additives with the best net emissions are identified.

GRAPHICAL ABSTRACT



INTRODUCTION

Force main (or pressure main) sewers are commonly employed as a part of sewer networks when gravity sewers are not possible/feasible. In force main sewers, the sewage is typically pumped from a wet well through enclosed pipes without headspaces, and this can lead to anaerobic conditions. The creation of anaerobic conditions can be further accentuated if sewage is pumped intermittently due to fluctuations in sewage flows (Hvitved-Jacobsen

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2002) or if flow velocities are sub-scouring and allow the deposition of solids and/or biofilm build-up (Li *et al.* 2015). The potential for the generation of hydrogen sulphide (H_2S) in force mains has been recognised for a considerable time as its presence can lead to strong odours and sewer pipe corrosion (Sharma *et al.* 2008; Zhang *et al.* 2023). More recently, the potential for the significant generation of methane (CH_4), which is a potent greenhouse gas (GHG), has been identified (Liu *et al.* 2015).

The dosage of additives into force mains for controlling H_2S discharges has been employed in practice is a widespread practice. There is a growing interest in the use of similar practices for controlling CH_4 generation (Jiang *et al.* 2013; Gutierrez *et al.* 2014; Auguet *et al.* 2015; Kiilerich *et al.* 2017; Despot *et al.* 2020; Zuo *et al.* 2020; Guo *et al.* 2023). However, not all additives have the same modes of action and hence the ability to extend from H_2S control to CH_4 control needs careful attention (Liu *et al.* 2015). In addition, all additives will have embodied GHG emissions associated with their manufacture and distribution. There has, however, been little discussion about the relative amounts of embodied emissions as compared with the CH_4 emissions that would be controlled by the use of the additives.

This paper initially reviews microbial processes leading to H_2S and CH_4 generation in sewers, factors that can influence their generation and concentrations that have been reported in force main effluents. The literature on common additives employed in force main sewers is reviewed with respect to their chemistry, commercially available formulations, modes of action in sewers and dosing practices. Literature reporting the embodied GHGs associated with these additives is reviewed and factors affecting these values (i.e., alternative manufacturing and sources of raw materials) are examined. The embodied emissions associated with their use are then estimated based on typical dosing scenarios into force main sewers reported in the literature. The computed embodied emissions are then compared with the range of GHG emissions that can be expected in the absence of dosing. The paper concludes with a qualitative overview of non-embodied emissions (i.e., those occurring in downstream sewers and Water Resource Recovery Facilities (WRRFs)).

H_2S AND CH_4 GENERATION IN FORCE MAIN SEWERS

Species involved and formation pathways

H_2S is primarily generated through dissimilative SO_4 reduction that is carried out by sulphate-reducing bacteria (SRB). This is an anaerobic respiration employing SO_4 as a terminal electron acceptor. H_2S dissociates at a pH value of 7 and hence at lower pH values the volatile form of H_2S is present (Rittmann & McCarty 2020). By comparison, CH_4 is produced either by acetoclastic or hydrogenotrophic methanogens, which are obligate anaerobes that belong to the Archaea kingdom. Acetoclastic methanogenesis involves the cleavage of acetate to form CH_4 and CO_2 , while hydrogenotrophic methanogenesis is achieved through anaerobic respiration using molecular hydrogen as the electron donor and CO_2 as the electron acceptor.

SRB and methanogens both employ volatile fatty acids and molecular hydrogen as growth substrates. These substances are generated as the byproducts of hydrolysis, fermentation and acidogenesis when wastewater containing complex organics are subjected to anaerobic conditions. There is a competition between the two groups of organisms for these substrates with SRB typically growing faster than methanogens. Hence, in biofilm systems, like those present in force main sewers, the SRB tend to predominate the surface layer of the biofilm while methanogens tend to be present in the base layers where longer solids residence times prevail (Liu *et al.* 2015).

Factors affecting H_2S and CH_4 generation

The generation of H_2S and CH_4 by anaerobic organisms in force mains are both impacted by a number of common factors including the availability of substrate and nutrients, alternative electron acceptors, temperature, hydraulic residence time, surface area to volume ratio and scouring velocity (Zhang *et al.* 2023). The principal impact of substrate and nutrients is increasing the growth and metabolism at the biofilm surface, with diffusion limitations being a controlling aspect. The presence of alternative electron acceptors like oxygen or nitrate will typically inhibit anaerobic processes either by supporting competition for growth substrates or directly inhibiting the anaerobic organisms. Both SRB and methanogens are mesophilic organisms and hence their growth in sewers typically increases as temperatures increase. The hydraulic residence time of sewage in force mains impacts the contact time between the sewage and the biofilm. As residence times increase, the uptake of substrates will increase and the associated production of products (H_2S and CH_4) can increase. The surface area to volume ratio increases as the diameter of the sewer decreases. Since biofilm activity will be proportional to the surface area, its impact on product concentrations in small-diameter sewers will be greater. Higher sewage

velocities result in less deposition of solids and thinner biofilms and hence support less active biomass. System factors that influence these factors will have similar impacts on both H₂S and CH₄ generation.

Some sewer conditions will impact H₂S and CH₄ generation differently and hence the demand for additives that mitigate generation may vary between locations (Zhao *et al.* 2022). The concentration of SO₄ in sewage can vary between locations, and its availability can impact the amount of H₂S that can be generated in a force main sewer. Furthermore, since SRB compete with methanogens for substrates, elevated SO₄ concentrations may reduce the generation of CH₄ in a sewer due to a lack of substrate. Hence, the quantities of additives that are needed to react with H₂S as a byproduct could vary between locations while the quantities required for CH₄ control may be less variable in this regard.

The pH value is a key environmental variable that influences the growth of microbes (Gutierrez *et al.* 2009). SRB and methanogens have somewhat different preferred ranges of pH values. SRB commonly prefer pH values in the range of 6.5–8, and some species can function at pH values that span 4–10. In contrast, methanogens tend to have a narrower preferred pH value range of 6.5–7.5. The pH value at which short-term biocidal effects are observed can differ from these preferred ranges, with the biocidal effects on SRB observed at pH values less than 4 or greater than 10, while the corresponding values for methanogens are between 5 and 9. Hence, the use of extreme pH values as a biocidal control for SRB in force mains will likely also be effective for methanogens, provided the high pH value penetrates deep into the biofilm.

H₂S and CH₄ concentrations in force main sewers

The generation of H₂S and CH₄ in force main sewers is substantially impacted by local factors and hence their concentrations at sewer outlets have been found to span a range of values. Table 1 summarises values that have been reported in the literature and reveals that their concentrations vary by about an order of magnitude, with similar levels of H₂S and CH₄. In studies that conducted temporal sampling (Sharma *et al.* 2008; Guisasola *et al.* 2009), it has been demonstrated that concentrations can vary temporally over a relatively short period of time (i.e., hours). This can be particularly important for force mains that have very low intermittent flows, and hence long hydraulic residence times (HRTs), through early morning hours. It was noted that a majority of studies reporting H₂S and CH₄ in full-scale force main sewers have been conducted in Australia, and there is little full-scale data reported from other regions.

Table 1 | Reported H₂S and CH₄ concentrations in full-scale force main sewers

H ₂ S concentration (g S/m ³)	CH ₄ concentration (g/m ³)	Reference
NA	1–9.3	Foley <i>et al.</i> (2009)
7.5–12	4.4–6.1	Guisasola <i>et al.</i> (2008)
5–10	3.5–15	Liu <i>et al.</i> (2015)
2.5–14	2.5–4	Gutierrez <i>et al.</i> (2014)
1–15	NA	Sharma <i>et al.</i> (2008)

ADDITIVES EMPLOYED FOR CONTROL OF H₂S AND CH₄ IN FORCE MAIN SEWERS

The generation of odours from reduced sulphur compounds and corrosion induced by sulphides has been recognised for about 70–80 years (Thistlethwayte 1972; Pomeroy 1974). Hence, there is a considerable body of knowledge that has been developed regarding the use of chemical additives to mitigate either hydrogen sulphide generation or emission in force mains. The impact of traditional sulphide-control chemicals and alternate chemicals on methane generation in force mains has only been investigated more recently. In this section, the more commonly employed chemicals are reviewed with respect to their chemistry, modes of action, dosing strategies and typical dosage ranges. Table 2 summarises dosages and dosing strategies that have been reported in the literature for common additives.

Nitrate

Nitrate is the anion of nitric acid, which is a strong acid with a pKa value of –1.3. Hence, it is typically deployed as a concentrated aqueous solution of sodium, calcium or potassium salts (e.g., 50% calcium nitrate solution). In the absence of dissolved oxygen, nitrate is used as the preferred electron acceptor by heterotrophs that employ

Table 2 | Prior use of additives in force main sewers for sulphide or methane control

Substance	Dosage (active ingredient)	Dosing strategy	Reference
Nitrate	30 mg/L NO ₃ -N	Continuous	Jiang <i>et al.</i> (2013)
Nitrite	20 mg/L NO ₂ -N	Continuous	Auguet <i>et al.</i> (2016)
Free nitrous acid	^a 100–230 mg NO ₂ -N/L HCl to lower pH to 6.2	Intermittent: 12 h/5 days	Jiang <i>et al.</i> (2011)
	^b 23 mg NO ₂ -N/L HCl to lower pH to 5.5	Intermittent: 12 h/14 days	Nguyen & Marano (2016)
pH elevation	88–120 mL of 0.05 M NaOH/L pH 8.6–9.0	Continuous	Gutierrez <i>et al.</i> (2009)
pH shock	520 mg NaOH/L pH 12.5	Intermittent: 6 h/week	Gutierrez <i>et al.</i> (2014)
Ferric iron	21 mg Fe/L	Continuous	Zhang <i>et al.</i> (2012)
Ferrous iron	0.53 L 5.15% w/w FeSO ₄ /m ³	Continuous	Kiilerich <i>et al.</i> (2017)
Calcium peroxide	0.1–0.2% w/v	Intermittent: 12 h/weekly basis	Guo <i>et al.</i> (2023)
Free ammonia	154 mg N/L pH 9.2	Intermittent: 24-h exposure	Zuo <i>et al.</i> (2020)
		– 6 days for H ₂ S – 28 days for CH ₄	

^aPilot scale testing results.^bCommercial scale use.

biodegradable organic matter as a growth substrate. Heterotrophs have substantially faster growth kinetics and greater yields than SRB or methanogens and hence will tend to dominate the surface layer of biofilms that develop in force mains if nitrate is available. Heterotrophic growth on nitrates will reduce the availability of readily biodegradable organic matter in sewers and hence limit the substrate availability for downstream generation of H₂S and CH₄ (Jiang *et al.* 2013). Heterotrophic growth on nitrates can also oxidise sulphide to elemental sulphur and polysulphides, which embed into the biofilm (Liang *et al.* 2016). Also, excess heterotrophic biomass sheds into the bulk water where it continues its metabolic activity. In high HRT force mains that receive nitrate treatment, substantial reductions in soluble biochemical oxygen demand (BOD) can be observed along with increases in volatile suspended solids (VSS). Further, the development of a thick layer of heterotrophic biomass on the outer layer of biofilms can reduce the transport of all substrates into the inner biofilm layers and thereby act as a physical barrier to substrate availability for H₂S and CH₄ generation. In addition, some SRB will utilise nitrate as an electron acceptor, when present, rather than sulphate and hence H₂S generation can be reduced in this manner. Nitrate can directly inhibit methanogens by disrupting enzymatic reactions involved in methanogenesis, leading to a decrease in methane production. Viewed collectively, dosing of nitrate into force mains can reduce H₂S and CH₄ generation through multiple mechanisms.

Nitrate is typically dosed continuously into force main sewers to mitigate H₂S as it does not have biocidal properties. The quantity of nitrate that is required will likely be determined by the demand exerted by heterotrophs which can become very high for sewer HRTs greater than 2 h. Modern dosing systems employ an H₂S sensor located at the force main discharge to inform a process controller that regulates the nitrate dosage. The dosage of nitrate into sewers has typically been in the range of 30 mg N/L (Table 2).

Nitrite

Nitrite is the anion of nitrous acid, which is a weak acid with a pKa value of 3.2. NaNO₂ is a commonly available salt of nitrite, which is relatively unstable when dissolved in water. Hence, systems that employ nitrite as an additive tend to make up the dosing solution from granular salt on site just prior to dosing. Ionised nitrite can act as electron acceptor by a variety of heterotrophs and hence can reduce H₂S and CH₄ generation in a manner similar to that of nitrate (Auguet *et al.* 2016). Studies that have evaluated the use of nitrite in this manner (Table 2) have reported a dosage of 20 mg N/L effectively reduced H₂S and CH₄ generation. When continuous dosing was employed, the higher costs of nitrite and the challenges of managing granular dosing systems tend to limit its application.

Nitrite can also be employed in the protonated form (free nitrous acid (FNA)). This typically requires lowering the pH value of the sewage (6–6.5) such that partial protonation of nitrite is achieved. FNA has been demonstrated to be highly toxic to SRB and methanogens. Intermittent FNA concentrations of 0.2–0.3 mg N/L applied over consecutive 24-h periods have been reported to inhibit both SRB and methanogen growth (Jiang *et al.* 2011). The strong biocidal effects of FNA support the use of alternative dosing strategies as residual inhibition will remain for a period of time after the exposure of microbes to FNA. Also, the removal of the biofilm retards sulphide production until such time the biofilm can re-establish, which takes longer for methanogens than SRBs. As indicated in Table 2, H₂S generation required 5 (bench scale) to 14 days (commercial scale) to rebound after a 12-h exposure at an FNA concentration of 0.26 mg N/L. Bench scale studies employed elevated doses of nitrite (230 mg N/L) at a pH value of 6.5 while the commercial scale implementation used a lower nitrite dose (23 mg/L), but the pH value was reduced to 5.5 to achieve similar FNA concentrations. FNA dosing into sewers requires a more complex dosing setup that includes onsite make-up of the nitrite and concurrent dosing of an acid (typically hydrochloric acid, HCl) to lower the pH value for protonation of the nitrite.

Elevated pH value

The pH value of the sewage in a force main is a key water quality characteristic that can impact the growth of all organisms. Continuous elevation of pH value (8.6–9) in sewers has been found to substantially inhibit the growth of SRB and methanogens. In addition, maintaining the pH value in this range will cause H₂S to deprotonate to form HS⁻ (pK_a = 7.0) which is considerably less volatile than H₂S and hence odour emissions associated with this compound can be reduced. Common chemicals employed to increase the pH value in force mains include NaOH (caustic), Mg(OH)₂ (milk of magnesia) and Ca(OH)₂ (lime). NaOH is commercially available in 50% solutions that can be directly dosed into a sewer, Mg(OH)₂ is typically added as a 60% slurry, while Ca(OH)₂ is used as a 45% slurry. The dosage required to elevate the sewage pH value will depend upon the composition of the wastewater, and Table 2 reveals that a dosage of approximately 5 mM NaOH was required in one instance.

While continuous increase to moderately high pH values has been found to be effective, it can be costly, and residual inactivation of organisms is limited if dosing is ceased. Hence, the use of pH shocking to higher pH values (10.5–12.5) for relatively short exposures (0.5–6 h) has been found to have residual biocidal effects after cessation of dosing. The biocidal effect of this mode of operation has been found to reduce H₂S generation for a week and methane generation for up to 4 weeks (Gutierrez *et al.* 2014). The benefits of pH shocking include reduced demand for (continuously fed) chemicals, less impacts of the chemical dosing on downstream systems like wastewater treatment and no need for onsite storage of chemicals. Care must be taken, however, to ensure that the high-pH spike is diluted before reaching the WRRF.

Iron

Iron has been traditionally employed in sewers for controlling sulphides in either ferric (Fe³⁺) or ferrous (Fe²⁺) forms. Ferric iron is commercially available as either FeCl₃ or Fe₂(SO₄)₃ at concentrations of 35–45% as a liquid. Ferrous iron is commercially available as a liquid as FeCl₂ or FeSO₄·7H₂O at concentrations of 35–40% and 40–50%, respectively. Both forms will react with sulphides to form precipitates and hence can eliminate associated odours and corrosion. When dosed into sewage, iron will react with water under neutral pH values to form relatively insoluble oxy-hydroxide precipitates and hence many reactions that occur in sewers (adsorption, bio-transformation, etc.) involve surface reactions that can reduce rates. Ferric iron can act as an alternative electron acceptor for some heterotrophic bacteria and hence the levels of readily available organics as substrates to SRB and methanogens can be reduced (Zhang *et al.* 2012). There is evidence that either form of iron addition can partially suppress methanogens in sewer biofilms although the mechanisms of suppression have not been conclusively delineated (Kiilerich *et al.* 2018). The accumulation of Fe precipitates in biofilms may be partially responsible for suppression as the increased density of the biofilm would tend to reduce the mass transfer of substrates into the depth of the biofilm where methanogens typically reside. Iron dosing needs to be maintained continuously to sustain the control of H₂S and CH₄ generation. The demand for iron dosing in sewers has typically been based on the quantities of sulphide that are generated with a typical ratio of 2.5 kg Fe/kg S employed.

Regenerating the added ferrous or ferric iron *in situ* through the addition of an oxidising agent (H₂O₂ or air/oxygen) has shown benefit in economising cost for controlling H₂S with iron (Nunez *et al.* 2010). However, because of the reduced iron dosage, the suppression of CH₄ generation is expected to be less.

Calcium peroxide

Calcium peroxide (CaO_2) is a highly reactive substance that decomposes to release oxygen, hydrogen peroxide (H_2O_2) and CaO when added to sewage (Xu *et al.* 2020). As such, CaO_2 addition to sewage can impact H_2S and CH_4 generation through several pathways. The introduction of oxygen into the sewage provides an electron acceptor for the growth of heterotrophs that will support the competitive pathways previously described for nitrate addition. H_2O_2 itself is an oxidant, and its decomposition in water leads to the formation of oxygen. Viewed collectively, the addition of CaO_2 to force main sewers can reduce the generation of H_2S and CH_4 through several pathways. The biocidal and particulate properties of CaO_2 support the use of intermittent dosing strategies (Guo *et al.* 2023). The use of 12-h exposures at 2% w/v on a weekly basis has been demonstrated to reduce H_2S and CH_4 generation in a force main by 80%.

Free ammonia

Free ammonia (NH_3) is the deprotonated form of ammonium (NH_4^+) that has a pKa value of 9.25. Hence, NH_3 will only be present in significant quantities in sewage at relatively high pH values. NH_3 has biocidal properties itself and the elevation of pH to create NH_3 from NH_4^+ can also result in some reduction of microbial activity. The biocidal properties of NH_3 can support the use of intermittent dosing strategies if the NH_3 concentrations are sufficiently high. A dosage of 154 mg N/L at a pH value of 9.2 for 24 h has been reported to result in an 80% reduction of H_2S and CH_4 generation for 6 and 28 days, respectively (Zuo *et al.* 2020). NH_4^+ is naturally present in sewage and hence some NH_3 can be formed by elevating the pH value of the sewage. However, supplementation of NH_4^+ would be required to achieve sufficient biocidal properties. It is unlikely that dosing of NH_4^+ into sewers would be acceptable in most applications due to the impacts on downstream wastewater treatment. Source diversion of urine has been suggested as an alternative scheme to supply NH_4^+ for free ammonia inhibition without creating a net increase of loadings to the sewer.

EMBODIED CO_2 EMISSIONS OF ADDITIVES

Additives that are employed for controlling H_2S and CH_4 generation in sewers are typically industrial chemicals that have embodied GHGs associated with raw material extraction, manufacturing and supply chain handling. In this section, the production of the previously described additives is reviewed, and the reported embodied GHG emissions are summarised. Table 3 summarises the embodied emissions of the common additives that have been reported in the literature.

Table 3 | Embodied GHG emissions associated with additives (Althaus *et al.* 2007)

Additive		Embodied emission
Nitrate		10.1 kg $\text{CO}_2\text{-e/kg N}$
Nitrite		13.75 kg $\text{CO}_2\text{-e/kg N}$
HCl		1.2 kg $\text{CO}_2\text{-e/kg HCl}$
Elevated pH	NaOH	0.46 kg $\text{CO}_2\text{-e/kg NaOH}$
	Lime	0.11 kg $\text{CO}_2\text{-e/kg Ca(OH)}_2$
Iron	Ferrous	0.15 kg $\text{CO}_2\text{-e/kg Fe}$
	Ferric	0.18 kg $\text{CO}_2\text{-e/kg Fe}$
Calcium peroxide		0.65 kg $\text{CO}_2\text{-e/kg CaO}_2$
Ammonia		4.1 kg $\text{CO}_2\text{-e/kg NH}_4\text{-N}$

Nitrate

The most common method for producing nitrates involves the oxidation of ammonia to form nitric acid, which can then be further converted to nitrates. The process typically consists of ammonia oxidation where ammonia gas is reacted with oxygen to produce nitrogen oxides (NO and NO_2), which are then absorbed (under pressure) into water to form nitric acid (APCA 1964). The generated nitric acid can be further neutralised with appropriate bases to produce different nitrates. The primary GHGs associated with nitrate manufacturing include carbon dioxide and nitrous oxide (N_2O). Carbon dioxide emissions are associated with fuel combustion for energy

while nitrous oxide emissions can occur due to fugitive losses from the ammonia oxidation and nitric acid production processes. In addition to these manufacturing-related emissions, the ammonia that is employed as a raw material has embodied carbon dioxide emissions. The primary source of these emissions is the synthesis gas production step, which involves the conversion of natural gas into hydrogen and carbon monoxide through steam methane reforming.

Nitrite

Sodium nitrite is typically manufactured by sodium nitrate reacting with sodium hydroxide in a solution. The resulting sodium nitrite solution undergoes purification and is then concentrated and dried to obtain sodium nitrite crystals (Laue *et al.* 2012). Hence, the GHGs associated with nitrite production include those with the manufacturing process as well as those embedded in nitrate and sodium hydroxide manufacturing. The primary GHGs associated with nitrite manufacturing include carbon dioxide and nitrous oxide. Carbon dioxide emissions are associated with fuel combustion for energy while nitrous oxide emissions can occur due to fugitive losses during manufacturing.

When nitrite is converted to FNA, HCl is typically added to lower the pH value and hence the embodied emissions associated with HCl manufacture should be included. HCl is commonly manufactured through the direct synthesis method in which hydrogen gas and chlorine gas react with the resulting HCl gas dissolved in water to form hydrochloric acid (Austin & Glowacki 2000). The GHGs associated with the manufacture of HCl include those embedded in hydrogen and chlorine gases and those associated with energy required for the manufacturing process.

Elevated pH

Strong bases such as NaOH, Mg(OH)₂ or lime are typically employed for pH elevation in sewers. The chloralkali process, which involves the electrolysis of a sodium chloride brine, is employed to produce sodium hydroxide and chlorine gas (Kumar *et al.* 2021). The sodium hydroxide is concentrated and purified to obtain solid sodium hydroxide. GHGs associated with the manufacturing of NaOH are those generated during the producing of electricity for the electrolysis process and with the sourcing of the NaCl.

Lime is typically manufactured by calcination of limestone at high temperatures. During calcination, carbon dioxide is released as a byproduct and the resulting lime is typically in the form of solid quicklime (National Lime Association 1992). GHGs associated with the manufacturing of lime are those generated during the sourcing of the raw limestone, produced during the combustion of fuels to provide heat for calcination and generated from the calcination itself. On an industrial scale, Mg(OH)₂ is produced by treating seawater with lime (Ca(OH)₂). The GHGs associated with Mg(OH)₂ are thus similar to those described for lime.

Iron

Iron is employed in either its ferric or ferrous states with either chloride or sulphate as the associated anion. Ferrous iron solutions are typically manufactured by dissolving iron (scrap steel) in either hydrochloric or sulphuric acids. Ferrous iron is also obtained as a waste material from titanium dioxide manufacture, where available. Similarly, spent pickle liquor is a byproduct of steel manufacturing that has high iron content and is employed as a source for ferrous iron. Ferric iron is generated by oxidising ferrous iron with chlorine gas (Wildermuth *et al.* 2000). There is increasing competition for scrap steel and hence manufacturing of iron solutions from iron ore may be necessary in the future. In this process, iron ore is initially converted to iron oxide by roasting the iron ore at elevated temperature in the presence of oxygen. The iron oxide is then dissolved in an acid solution (hydrochloric or sulphuric) to produce a ferric iron solution.

GHGs associated with the preparation of iron solutions will vary substantially depending on whether scrap iron or iron ore are employed as raw materials. Production of GHGs when scrap steel is used as an iron source is associated with the energy needed to transport and handle scrap steel, raw materials (acids, chlorine) and energy consumed when dissolving the iron in an acid solution. The production of GHGs when iron ore is used includes those generated from energy use during ore mining and transportation, processing (crushing, etc.), roasting in high-temperature furnaces and iron oxide dissolution in acid solution. Emissions associated with other raw materials (acids and chlorine) employed in iron dissolution will also be generated.

Calcium peroxide

Calcium peroxide is manufactured by reacting lime with hydrogen peroxide at elevated temperatures (Jakob *et al.* 2007). The solid calcium peroxide is typically dried to remove residual moisture. GHGs associated with calcium peroxide manufacturing include those embodied in lime and hydrogen peroxide manufacture as well as those associated with the energy needed to complete the reaction between lime and hydrogen peroxide (heating, mixing, etc.).

Free ammonia

Ammonia is primarily manufactured through a process called the Haber–Bosch process, which involves the synthesis of nitrogen and hydrogen gases (Appl 2011). Nitrogen is typically obtained from air while hydrogen is produced using natural gas. This process takes place under high pressure and moderate temperature. The Haber–Bosch process is energy-intensive, and the production of hydrogen gas from natural gas generates considerable carbon dioxide emissions. Additional emissions are associated with the energy required for process heating and fugitive emissions of nitrous oxide if process conditions are not optimised.

EMISSIONS ASSOCIATED WITH TYPICAL DOSING SCENARIOS

The emissions associated with dosing additives for controlling H₂S and CH₄ generation were computed as the product of dosages that have been reported to be effective (Table 2) and the embodied emissions associated with the additives (Table 3). The computation of the emissions (Table 4) accounted for differences in dosing strategies. In the case of additives that are continuously dosed into the sewer, the emissions were computed as the direct product of the dosage and the emission factor to obtain an emission per unit volume of wastewater. In the case of additives that are intermittently dosed into the sewer (i.e., those with residual biocidal properties), the average dose into the sewer over an entire dose cycle was employed in the calculation of the average emission per unit volume of wastewater.

Table 4 | Estimated CO₂ emissions associated with dosing of additives

Substance	Average dose	Embodied CO ₂ -e	Emission (mg CO ₂ -e/L)	Net emissions ^a (mg CO ₂ -e/L)
Nitrate	30 mg NO ₃ -N/L	10.1 mg CO ₂ /mg NO ₃ -N	303	83
Nitrite	20 mg NO ₂ -N/L	13.75 mg CO ₂ /mg NO ₂ -N	275	55
Free Nitrous Acid (Nitrite + HCl)	23 mg NO ₂ -N/L + 16.5 mg HCl/L	13.75 mg CO ₂ /mg NO ₂ -N + 1.2 mg CO ₂ /mg HCl	336	116 ^b
	0.8 mg NO ₂ -N/L + 1.2 mg HCl/L	13.75 mg CO ₂ /mg NO ₂ -N + 1.2 mg CO ₂ /mg HCl	12.7	-207 ^c
pH elevation (Ca(OH) ₂)	220 mg Ca(OH) ₂ /L	0.11 mg CO ₂ /mg Ca(OH) ₂	24.2	-196
pH shock	20 mg Ca(OH) ₂ /L	0.11 mg CO ₂ /mg Ca(OH) ₂	2.2	-218
Ferric iron	21 mg Fe/L	0.18 mg CO ₂ /mg Fe	3.8	-216
Ferrous iron	27 mg Fe/L	0.15 mg CO ₂ /mg Fe	4.0	-216
Calcium peroxide	140 mg/L	0.65 mg CO ₂ /mg CaO ₂	91	-129
Free ammonia	22 mg NH ₄ -N + 20 mg Ca(OH) ₂ /L	4.13 mg CO ₂ /mg NH ₄ -N + 0.11 mg CO ₂ /mg Ca(OH) ₂	93	-127

^aAssuming average methane generation of 220 mg CO₂-e/L for the baseline (untreated) condition.

^bBased on pilot scale implementation at a pH value of 6.5.

^cBased on commercial implementation at a pH value of 5.5.

Table 4 reveals a substantial range in the embodied emissions associated with the dosing of additives. Emissions associated with the continuous use of nitrate and nitrite are the highest (275–303 mg CO₂-e/L) and are attributed to the relatively high emissions embodied in these additives. In contrast, biofilm shocking through the use of FNA (commercial scale implementation data) or alkali results in much lower net emissions due to the intermittent dosing strategies employed for these chemicals. The dosing of iron also has relatively low

emissions (3.8–4.0 mg CO₂-e/L). It should be noted that the values employed for the embodied emissions of iron were based on their sourcing from scrap iron. Should the availability of scrap iron decline and iron ore become the established source of iron, then it can be expected that these emissions will increase substantially.

The net emissions associated with the various additives were calculated as the difference between the embodied emissions of the additives and the emissions that were estimated to be generated in force main sewers without additives. The studies cited in Table 1 indicate that CH₄ concentrations in force main effluents have ranged between 1 and 15 mg/L. CH₄ has a global warming potential of 28 g CO₂/g CH₄ (IPCC 2013), and if all of the generated methane were to be stripped into the atmosphere, the equivalent emissions per unit volume of wastewater would be 28–420 mg CO₂-e/L. A comparison of the values for embodied emissions associated with additives (Table 4) with this range of potential CH₄ emissions indicates that some of the additives (i.e., most N-based substances) will have relatively little impact on net GHG emissions. For these additives, the embodied emissions will be equivalent to or greater than the CH₄ emissions generated in their absence. Conversely, the use of biofilm shocking techniques (particularly with lime), or iron-based additives, could result in substantial reductions in net GHG emissions as their embodied emissions are likely less than the generated CH₄ emissions. In these cases, the net emissions were determined to have a negative value implying a net reduction in emissions with additive use.

The use of additives for CH₄ emissions control should be considered in context with their traditional use for H₂S control. Iron-based additives have traditionally been employed for H₂S control due to the chemical reactivity between iron and H₂S. There is, however, a limited database describing their effectiveness for CH₄ control, and further studies over a range of operating conditions should be completed before employing them for this purpose, as iron-based additives are not strongly biocidal. In contrast, pH shocking is relatively well-understood, and the biocidal nature of this approach should achieve a high level of CH₄ control if H₂S control is achieved consistently. Methanogens are known to be slower-growing than SRB and tend to be sensitive to environmental perturbations to pH. Hence, monitoring and control systems that are effective for H₂S control could be employed to ensure that methane generation is limited. Furthermore, integrating an intermittent biofilm shocking component into a continuous-feed iron-based program would be expected to reduce sulphide control costs while addressing GHG emissions from sewers.

NON-EMBODIED EMISSIONS ASSOCIATED WITH ADDITIVE USE

The choice of H₂S and CH₄ control chemicals can also affect the GHG footprint indirectly through the transformation and/or disposition of the additives in the downstream sewer and WRRF. As there are many system-specific variables that influence the impact of the additives, this section presents a qualitative assessment of these emissions.

The use of nitrate as an additive can have several downstream impacts. Most directly, denitrification reactions following nitrate addition are likely to result in N₂O generation and subsequent emissions from naturally aerated gravity mains downstream of force main discharges (Beaulieu *et al.* 2010). In addition, nitrate consumption in the biofilm converts soluble carbon into cell mass, which adds to influent TSS/VSS but can be diverted through primary clarification into the solids' stream. For conventional activated sludge plants, this carbon diversion results in lower blower demand and less electricity use. For biological nitrogen removal plants that employ denitrification, this removal of soluble carbon by nitrate dosing means that supplemental carbon may need to be purchased for the denitrification step (Kobylnski *et al.* 2010). The GHG footprint of the purchased carbon should thus be assigned to the nitrate dosed into the collection system. Concurrent with soluble carbon uptake by the biofilm is alkalinity production, which is needed in the nitrification step of the biological nitrogen removal process. In this case, nitrate use within the collection system can reduce the amount of NaOH, Mg(OH)₂ or Ca(OH)₂ purchased for WRRF operations, and so lower the associated GHG footprint. When dosed continually into the collection system, nitrite addition will impact the WRRF similarly to nitrate. When dosed intermittently (as a biofilm shocking agent), the GHG impacts at the WRRF are minimal and transient.

For biological nitrogen removal plants, alkalinity added in the collection system to elevate pH can offset alkalinity added at the WRRF (needed in the nitrification step). In this case, NaOH, Mg(OH)₂ or Ca(OH)₂ use within the collection system can reduce the amounts purchased for WRRF operations and lower the associated GHG footprint.

Iron is unique among the evaluated chemicals in its impact on WRRF operations (Rebosura *et al.* 2018). This can be attributed to its elemental nature and its capacity to cycle between two valence states (Fe²⁺ and Fe³⁺). This

cycling drives the interactions of iron with sulphur and phosphorous, which can be managed by oxygenation with air, oxygen or hydrogen peroxide (Wilfert *et al.* 2015). In terms of the GHG footprint, iron dosing in sewers can impact chemically enhanced primary treatment and/or chemical phosphorous removal processes that divert carbon to the solids stream where it can be converted into biogas, instead of consuming blower and aeration capacity in the water line. If fermentation or digestion processes are employed for sludge stabilisation, they will benefit from iron dosing as it can control both biogas H₂S and struvite scaling through precipitation of sulphide and phosphate, respectively, as well as enhance volatile solids destruction. The GHG benefits include more biogas production (potential for renewable natural gas (RNG) credit) and less CO₂ production associated with a reduction in organic residue landfilled, land-applied or dried/incinerated. Finally, dewatering of digested solids benefits from iron dosing as it can control odours and retain phosphate in the dewatered cake, removing it from return flows to the water line.

For economic reasons, calcium peroxide use in the collection system is limited to intermittent biofilm treatments. Consequently, its GHG impacts at the WRRF are minimal and transient. Similarly, ammonia use in the collection system has historically been limited, intermittent or incidental. Adding ammonia to sewers would negatively impact electrical/blower costs (and the GHG footprint) due to the additional aeration requirements associated with nitrification.

When viewed collectively, it is apparent that sewer additives can have system-wide impacts on GHG emissions. An analysis of such impacts would need to carefully consider the interactions between the additives and the downstream chemical and biochemical processes in sewers, wastewater and sludge treatment. While these types of analyses are feasible, comprehensive tools for performing such assessments do not exist. The development of such tools to support these assessments would assist in the identification of optimal solutions on a system-wide basis.

CONCLUSIONS

Microbial processes leading to H₂S and CH₄ generation in sewers and the factors that can influence their generation and concentrations that have been reported in force main effluents in the literature were reviewed. The literature on common additives employed in force main sewers was reviewed with respect to their chemistry, commercially available formulations, modes of action in sewers and dosing practices. The embodied GHG reported in the literature for these additives were summarised. The embodied emissions associated with their use were estimated based on typical literature-reported dosing scenarios into force main sewers and net emissions considering GHG emissions that can be expected in the absence of dosing were calculated. The results revealed that biofilm shocking techniques and iron addition have the greatest net reduction in GHG emissions from force main sewers. There is, however, uncertainty associated with the mechanisms by which iron reduces CH₄ generation in force mains. Furthermore, future changes in the sourcing of iron that require the use of iron ore may increase the embodied emissions associated with this additive. A qualitative assessment of non-embodied emissions (those occurring in downstream sewer and WRRF) revealed that these impacts are additive and system-specific. The development of tools for assessing the system-wide impacts of additive use on GHG emissions would be beneficial.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

CONFLICT OF INTEREST

The authors declare there is no conflict.

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First received 19 September 2023; accepted in revised form 30 November 2023. Available online 13 December 2023