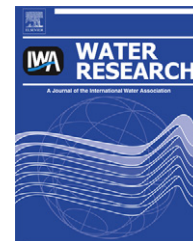


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Methane emission during municipal wastewater treatment

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ABSTRACT

Municipal wastewater treatment plants emit methane. Since methane is a potent greenhouse gas that contributes to climate change, the abatement of the emission is necessary to achieve a more sustainable urban water management. This requires thorough knowledge of the amount of methane that is emitted from a plant, but also of the possible sources and sinks of methane on the plant. In this study, the methane emission from a full-scale municipal wastewater facility with sludge digestion was evaluated during one year. At this plant the contribution of methane emissions to the greenhouse gas footprint were slightly higher than the CO₂ emissions related to direct and indirect fossil fuel consumption for energy requirements. By setting up mass balances over the different unit processes, it could be established that three quarters of the total methane emission originated from the anaerobic digestion of primary and secondary sludge. This amount exceeded the carbon dioxide emission that was avoided by utilizing the biogas. About 80% of the methane entering the activated sludge reactor was biologically oxidized. This knowledge led to the identification of possible measures for the abatement of the methane emission.

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1. Introduction

During wastewater treatment, the greenhouse gases carbon dioxide (CO₂), methane (CH₄) and nitrous oxide (N₂O) can be emitted to the atmosphere (Hofman et al., 2011). Carbon dioxide is produced indirectly as a result of fossil fuel combustion to generate the energy required for the operation of the wastewater treatment plant, or it is produced directly during the respiration of organic matter. In the latter case it concerns short-cycle carbon dioxide that does not contribute to increased atmospheric carbon dioxide concentrations. Nitrous oxide is expected to be emitted during biological

nitrogen removal from wastewater, through nitrification and subsequent denitrification (Kampschreur et al., 2009). Since nitrous oxide has a global warming potential of 300 CO₂-equivalents over a 100 year time horizon (IPCC, 2007), even a low emission contributes significantly to a WWTP's greenhouse gas footprint. Not in the least due to its high impact, nitrous oxide emission from wastewater treatment processes recently received a lot of attention. Methane, having a global warming potential of 25 CO₂-equivalents over a 100 year time horizon, is expected to be formed in the sewer system (Guisasola et al., 2008) and in those parts of the WWTP where anaerobic conditions prevail. Hitherto, the emission of

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methane from wastewater treatment received far less attention than the nitrous oxide emission.

Only two peer reviewed studies investigated the methane emissions of municipal wastewater treatment plants with activated sludge. Both studies used grab sampling to monitor the emissions. Czepiel et al. (1993) studied a small (12,500 PE) WWTP in Durnham, New Hampshire, USA; while Wang et al. (2011) investigated the methane emission from a large plant (1,500,000 PE) in Jinan, China. These WWTPs had no anaerobic digestion facility. The Dutch Foundation for Applied Water Research monitored methane emissions on three wastewater plants: Papendrecht (40,000 PE), Kortenoord (100,000 PE) and Kralingseveer (360,000 PE) (STOWA, 2010). The latter plant – which is also the subject of the present study – had an anaerobic sludge digestion facility, while the former two did not. The reported results from these studies are presented in Table 1. The share of methane in the total greenhouse gas emission from wastewater handling can amount up to 75% expressed as CO₂-equivalents (Foley and Lant, 2007).

Methane is emitted from a WWTP after it enters the plant via stripping from the incoming wastewater, or after it is formed at the plant itself. The influent of a WWTP contains dissolved methane that is formed in the sewer system. Recent studies indicate that methane formation in sewer systems can be substantial (Foley et al., 2009; Guisasola et al., 2008), but actual quantities of methane entering a WWTP have as yet not been reported. As far as methane production at the plant itself is concerned, it can be expected that in anaerobic zones, sludge thickeners and buffer and storage tanks methane is formed. In plants equipped with a digester for the anaerobic digestion of the surplus sludge, this can be expected to be a major source of methane. The biogas from the digester is usually combusted in a gas engine or flared, resulting in methane emissions with the off-gas (Liebetrau et al., 2010; Woess-Gallasch et al., 2010). Dissolved methane that leaves the digester, sludge thickeners and storage tanks will either be stripped during downstream processing (e.g. dewatering of the digested sludge) or will remain dissolved in the reject water and as such it will end up in the aeration tanks of the WWTP, as does the methane in the influent stream. There it

can be stripped during aeration, or it can be biologically oxidized by the microorganisms in the activated sludge. The potential methane oxidation of activated sludge systems has, to the authors' best knowledge, not been reported in the literature.

The objective of this study was to determine the contribution of methane to the greenhouse gas footprint of a wastewater treatment plant and to suggest measures to curb methane emissions. To obtain these goals, a one-year measurement campaign was carried out. The WWTP under study is fully covered, except for the secondary settling tanks, and all ventilation air is discharged through one stack. Gas measurements allowed estimation of total methane emissions, except for the exhaust of the biogas-based combined heat and power facility. Mass balances were used to reveal the sinks and sources of methane in this WWTP. Therefore, additional gaseous and liquid sampling was performed. To achieve reliable liquid sampling particular attention was paid to the sampling method.

2. Materials and methods

2.1. Wastewater treatment plant process scheme

The measurements and sampling were done at Kralingseveer WWTP, located in the municipality of Capelle aan den IJssel, near Rotterdam, the Netherlands (51° 54' 30" N 4° 32' 35" E). The plant treats the domestic wastewater of 360,000 population equivalents (PE). The excess sludge of the plant is treated in an anaerobic digester, operating at 34 °C. The resulting biogas is used in a combined heat and power installation that fulfills about 60% of the energy requirements of the plant. The remainder of the plant's energy needs is met by electricity and natural gas from the grid.

Kralingseveer WWTP receives mainly domestic sewage, with an average COD concentration of 339 mg L⁻¹, an average Total Kjeldahl Nitrogen concentration of 41 mg L⁻¹ and an average phosphorous concentration of 6 mg L⁻¹. The removal efficiencies are 87%, 92% and 77%, respectively. The average sludge loading rate was 0.21 kg COD kg VSS⁻¹ d⁻¹.

Table 1 – Normalized methane emissions for the present study and the other full-scale studies found in literature, as well as the methane emission factors used in the Netherlands by VROM.

	g CH ₄ person ⁻¹ year ⁻¹	kg CH ₄ (kg COD _{influent}) ⁻¹	g CH ₄ (m ³ influent) ⁻¹
Present study	306	1.13%	3.44
Czepiel et al. (1993) ^a – Durnham WWTP	39	0.16% ^b	0.14
Wang et al. (2011) ^a – Jinan WWTP	11	0.08%	0.16
STOWA (2010) – Papendrecht	266	0.87%	2.44
STOWA (2010) – Kortenoord	140	0.53%	1.56
STOWA (2010) – Kralingseveer (October)	310	1.20%	2.73
STOWA (2010) – Kralingseveer (February)	230	0.80%	2.03
VROM (2008)		0.85%	
WWTP with anaerobic sludge digestion			
VROM (2008)		0.70%	
WWTP without anaerobic sludge digestion			

a Based on grab samples.

b Expressed as kg CH₄ (kg BOD₅)⁻¹.

Fig. 1 displays the WWTP’s process scheme, while an aerial picture of the plant with the different unit processes is provided in Supplementary material 1. The incoming wastewater first passes through a bar screen and subsequently it goes to a primary settler. The primary sludge is sent from the primary settler to a gravitary thickener. The understream of the thickener is fed to the anaerobic digester, while the supernatant is returned to the primary settler. The water from the primary settler enters a selector (4800 m³) and from there it goes to an activated sludge reactor. This tank is a plug flow reactor that consists of an anoxic part for denitrification (3600 m³) and an aerated part for nitrification (8,000 m³). The aeration is achieved with bubble aeration. From the aerated zone, the mixed liquor is recycled to the anoxic zone at a recycle ratio of three. From this plug flow reactor, the mixed liquor flows into two parallel carousel reactors (2 × 13,750 m³) that are aerated with surface aerators. From the carousels, the mixed liquor goes to the secondary clarifiers. The secondary sludge from the clarifiers is partially recycled to the selector and the anoxic part of the second activated sludge system, while the waste sludge is fed to a belt thickener and subsequently to the anaerobic digester, together with the thickened primary sludge. Coming from the digester, the digested sludge is stored in a buffer tank with a maximum residence time of

five days and from there it goes to a centrifuge. The dewatered sludge is stored in a storage tank, from where it is loaded on a truck for transport to an incineration facility. The reject water from the belt thickener and the centrifuge are returned to the primary settler.

Except for the secondary clarifiers, all process elements of this WWTP are covered in order to collect the off-gas for gas treatment. Apart from the off-gas coming from the plug flow reactor and the carousel, all off-gas is collected and first directed to a compost filter to avoid odor nuisance. The air coming from the compost filter is blown into the headspace of the covered carousel reactor. The off-gas from the plug flow reactor and the carousel are finally disinfected in an ozone washer before it is released through the flue gas stack. Since the air coming from the compost filter is used to aerate the carousel, the gas flow to the ozone washer makes up the off-gas of the entire plant (except for emissions from the secondary clarifiers).

2.2. On-line measurements of the plant’s total off-gas

From 14 October 2010 until 28 September 2011, gas was withdrawn from the off-gas pipes going from the carousel and the plug flow reactor to the ozone washer. After passing

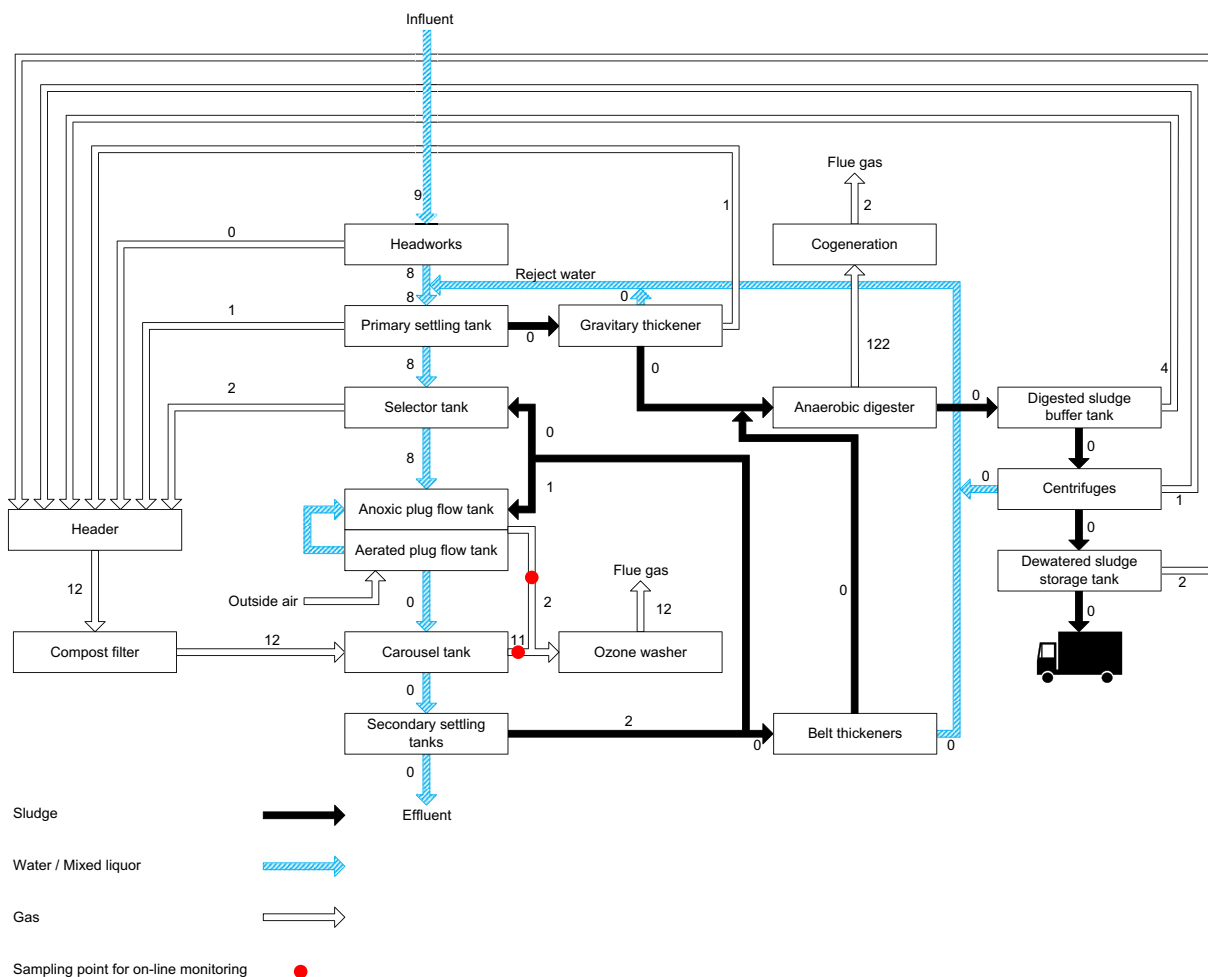


Fig. 1 – Process scheme of the Kralingseveer WWTP with the estimated mass flow rates (kg CH₄ h⁻¹) between the different unit processes.

through a condenser, the gas was directed to an on-line Servomex 4900 infrared gas analyzer, resulting in an estimation of methane in the overall off-gas flow leaving the water line and the sludge line of the plant. The gas flow rates in the off-gas pipes were measured weekly using a Tesco 435 hot wire anemometer. Since the blowers of the off-gas collection system were operated at constant power, the gas flow rates were constant. By multiplying the measured concentrations with the prevailing flow rate in the off-gas pipes, the methane fluxes from the plug flow reactor and the carousel were calculated.

2.3. Mass balances over each unit process

In order to identify the sources and sinks of methane on the plant, a mass balance was set up over each unit process. Therefore, the methane load in every single liquid and gas stream had to be calculated from the measured flow rates and corresponding concentrations. A detailed overview of these calculations is provided in [Supplementary material 2](#). The required measurements and sampling took place five times between 4 March and 12 August 2011, except for the exhaust gas of the cogeneration unit, which was measured only once. Flow rates of the gaseous streams were measured using an anemometer, while gas samples were collected with gas bags. The concentration of the content of the gas bags was measured with a Varian 3800 gas chromatograph equipped with a flame ionization detector (GC-FID). Flow rates of liquid streams were either available from the plant's SCADA system, or could be calculated from available data. Dissolved methane concentrations were measured with the salting-out method described below. For each stream, the methane loads determined during the five measurement campaigns were averaged.

For each unit process, the difference between the average methane load coming in and going out is the amount of methane that is produced or converted. In other words, it is possible to identify sources and sinks of methane on the plant, respectively. A unit process was only positively identified as a methane source or sink if the standard deviation of the load was smaller than the methane production or consumption.

2.4. Salting-out method for sampling methane in the liquid phase

For sampling dissolved methane, the salting-out method of [Gal'chenko et al., \(2004\)](#) was slightly adapted. The protocol that was used in this study can be found in [Supplementary material 3](#). Before the start of each sampling round, serum bottles of 120 mL were filled with 20 g NaCl. At the different sampling locations at the WWTP, samples were collected with a sampling beaker. From this beaker, 50 mL of sample was added carefully to a serum bottle filled with salt, using a syringe with a catheter tip and a 10 cm silicone tube. While emptying the syringe into the bottle, the silicon tube was held under the rising liquid surface in order to keep the liquid–gas interface as small as possible to avoid stripping. Immediately after adding the syringe content to the bottle, the bottle was sealed with a rubber stopper and an aluminum cap. The sealed bottle was shaken vigorously in order to speed up the dissolving of the salt.

At 20 °C the solubility of NaCl in water is about 360 g L⁻¹, so these samples, containing 400 g NaCl L⁻¹, were over-saturated. As a consequence of the high salt concentration, the microbial activity in the sludge samples is halted, and the dissolved gases are salted out. [Gal'chenko et al., \(2004\)](#) also added potassium hydroxide and/or merthiolate to the sample as a bactericide, but this was omitted in the samples from the WWTP since high salt concentrations (even far below saturation) are known to inhibit microbial activity both in the activated sludge ([Pernetti and Di Palma, 2005](#); [Zobell et al., 1937](#)) and in the anaerobic digestion process ([Feijoo et al., 1995](#)).

Dissolved methane, but also the other dissolved gases such as carbon dioxide escape from the liquid phase to the headspace of the serum bottles. This results in a pressure build-up in the headspace. [Gal'chenko et al., \(2004\)](#) neglected this pressure build-up, but for the samples of the present study, the pressure build-up was clearly noticeable since they contained substantially higher amounts of dissolved gases. Therefore it was necessary to take into account the pressure build-up due to the salting-out of the dissolved gases. Before sampling the headspace of the samples for analysis with GC-FID, the pressure in the headspace was equilibrated with the atmosphere by allowing the gas in the headspace to expand in a submerged graduated syringe. The increase in gas volume was used to calculate the pressure build-up in the headspace.

After the gas pressure in the headspace was brought to atmospheric pressure, the headspace was sampled with a gas syringe and analyzed. The amount of methane in the headspace before expansion was calculated from the concentration, the measured volume of the headspace of the sealed bottle and the headspace pressure after the pressure build-up that was calculated from the volume expansion of the headspace. Before the sample was saturated with salt, this amount of methane was completely dissolved in the liquid sample. By dividing this amount by the sample volume (50 mL) the original methane concentration in the liquid was established.

In order to compare the salting-out method with another method that had been used to sample dissolved methane, seventeen liquid streams with a solids content that was low enough to allow easy filtering were sampled using both the salting-out method of the present study and the vacuum tube method of [Guisasola et al. \(2008\)](#). According to the latter method, a syringe was filled with the sampled liquid. With a syringe driven filter unit and a hypodermic needle, the liquid was injected in an 11 mL Vacutainer blood serum tube (BD Diagnostics #367896). With a sample volume of 5 mL, ca. 97% of the methane is transferred to the headspace ([Guisasola et al., 2008](#)). The headspace was sampled with GC-FID. The amount of methane in the Vacutainer was calculated using Henry's law and a mass balance. The volume of the sample in the Vacutainer was determined by weight. This validation was also performed in the laboratory by sampling two prepared solutions of methane dissolved in water with both the salting-out method and the vacuum tube method. The solutions had an approximate concentration of 0.5 and 2.5 mg L⁻¹. For each solution and for each method, sampling was done in triplicate.

It was observed that empty Vacutainers after equilibrating with the atmosphere already contained about 400 ppm of methane. This methane possibly originated from the clot

activator coating on the inside of the tube wall. In order to verify this, a number of uncoated Vacutainer urine collection tubes (BD Bioscience #364915) were tested for the presence of methane. Also these uncoated tubes contained about 400 ppm of methane. These measurements were done with GC-FID, and corroborated with the infrared gas analyzer that was used for the on-line methane measurements at the WWTP. Both in the field and in the laboratory validation, the total amount of methane in the sample tubes was reduced with the average amount of methane that was measured in six empty Vacutainer tubes.

3. Results

3.1. Total methane emission from the WWTP

The daily average methane emission from the entire treatment plant at Kralingseveer during the measuring campaign (from 14 October 2010 until 28 September 2011) was $302 \text{ kg CH}_4 \text{ d}^{-1}$, with a standard deviation of $83 \text{ kg CH}_4 \text{ d}^{-1}$. The reported total methane emission comprises all methane in the off-gas that is collected in the plant's ventilation system and sent to the ozone washer, but the plant has two parts of which the off-gas is not collected for disinfection in the ozone washer: the uncovered secondary settlers and the exhaust of the gas engines of the cogeneration plant. The secondary settlers may emit some methane, but from the mass balance over the secondary settlers it appears that this amount will be very low (Table 2). The measured methane slip due to incomplete combustion in the gas engines was 1.3%, resulting in an additional methane emission of $38 \text{ kg CH}_4 \text{ d}^{-1}$.

The Dutch Ministry of Housing, Spatial Planning and the Environment (VROM, 2008) provided emission factors that are based on the IPCC inventory guidelines (IPCC, 2006). In order to allow comparison with these emission factors and with the results from other studies, the plant's total methane emission can be normalized in several ways: by population served, by wastewater flow or by incoming COD. Table 1 summarizes the resulting emission factors, as well as the emission factors from the other reported full-scale studies and the VROM emission factors. Apparently, about 1% (0.53–1.20%) of the incoming COD is emitted as methane in the Dutch treatment plants. At the Durnham plant, 0.16% of the incoming BOD_5 was emitted as methane, while at the Jinan plant, the emission factor was 0.08% of the incoming COD.

3.2. Sinks and sources of methane

All the methane containing streams of the WWTP are summed up in Table 2, while Fig. 1 shows the Kralingseveer WWTP lay-out with the estimated methane mass flow rates between the different unit processes. Using these mass flow rates, mass balances of methane were constructed over every unit process. From these mass balances, sources and sinks of methane could be identified.

For sampling dissolved methane, a method was used that consisted of salting-out the methane and analyzing the headspace of the recipient with gas chromatography. The method was validated by sampling a number of streams with both the

salting-out method and with a vacuum tube method. Fig. 2 shows the result for the validation. The results obtained by both methods correlate extremely well ($R^2 = 0.99$). The validation in the laboratory also yielded satisfactory results (Table 3).

Sources of methane at the plant itself are the primary sludge thickener, the exhaust gas of the cogeneration plant, the buffer tank for the digested sludge and the storage tank for the dewatered sludge. The latter two contribute substantially to the methane emission from the plant. From Table 2, it can be calculated that the buffer tank is responsible for $40 \pm 15\%$ of the emission from the carousel reactor and $35 \pm 13\%$ in the total methane emission, while the dewatered sludge storage tank has a share of $17 \pm 8\%$ in the emission from the carousel and $15 \pm 6\%$ in the total methane emission. Expressed as specific methane production rate, the buffer tank for the digested sludge produced about $3.5 \text{ g CH}_4 \text{ kg}^{-1} \text{ TSS d}^{-1}$, while the storage tank for the dewatered sludge produced about $1 \text{ g CH}_4 \text{ kg}^{-1} \text{ TSS d}^{-1}$. To compare, the digester had a production rate of $9 \text{ g CH}_4 \text{ kg}^{-1} \text{ TSS d}^{-1}$.

Besides the methane produced on the plant itself, methane also enters the plant from outside via the influent. The influent contains methane that has been formed in the sewer. The methane load was estimated as 1% of the influent COD load. From the measurements it was clear that a significant amount (roughly 80% of the dissolved methane in the influent, cf. Table 2 and Fig. 1) of methane is oxidized in the plug flow reactor. From Fig. 3 it appears that methane was removed in the aerated part of the plug flow tank only.

3.3. Methane emission dynamics

Fig. 4 shows the variation of the daily average methane emissions from the full treatment plant during the entire measurement period. Of the total methane emission, about 12% on average comes from stripping of methane in the plug flow reactor, while the remaining 88% is coming from the headspace of the carousel reactor. The methane in the off-gas from the plug flow reactor is only methane that is stripped after it enters the tank, since the tank is aerated with fresh air only. The emission from the carousel reactor is higher than the emission from the plug flow reactor, because the carousel is aerated with methane containing air coming from the compost filter. The compost filter treats the off-gas from all covered parts of the plant, except for the plug flow and the carousel reactor. It can reasonably be expected that that most of the methane coming from the carousel reactor is effectively derived from this ventilation air.

Fig. 5 shows the on-line methane emission from the plug flow reactor and the on-line flow rate of the influent. The graph shows the diurnal variation of both variables during one arbitrary week in the measurement period. The coefficient of determination R^2 between influent flow rate and methane emission from the plug flow reactor was 0.20 for the entire measurement period.

Fig. 6 compares the on-line methane emission from the carousel reactor, which amounts to the off-gas from the ventilation system, with the on-line sludge content of the dewatered sludge storage tank. Again, the graph shows an arbitrary week in the measurement period. For the entire measurement period, the linear correlation (R^2) between the

Table 2 – Methane mass balances over the various unit processes (kg CH₄ h⁻¹).

	In		Out		Balance
		$\bar{x} \pm \sigma$		$\bar{x} \pm \sigma$	$\bar{x} \pm \sigma$
Headworks	Influent	9 ± 3	Water to primary settling tank	8 ± 3	
			Off-gas	0 ± 0	
	Total	9 ± 3	Total	8 ± 3	-1 ± 4
Primary settler	Water from headworks + reject water from centrifuges, belt thickeners and gravitary thickener for primary sludge	8 ± 2	Water to selector tank	8 ± 3	
			Primary sludge	0 ± 0	
			Off-gas	1 ± 1	
	Total	8 ± 2	Total	9 ± 3	2 ± 4
Selector	Water from primary settling tank	8 ± 3	Liquor to plug flow reactor	8 ± 3	
	Return sludge	0 ± 0	Off-gas	2 ± 1	
	Total	8 ± 3	Total	9 ± 3	1 ± 4
Plug flow reactor	Liquor from selector	8 ± 3	Liquor to carousel reactor	0 ± 0	
	Return sludge	1 ± 1	Off-gas	2 ± 1	
	Total	9 ± 3	Total	2 ± 1	-7 ± 3
Carousel reactor	Liquor from plug flow reactor	0 ± 0	Liquor to secondary settling tank	0 ± 1	
			Off-gas	11 ± 3	
	Total	12 ± 3	Total	11 ± 3	-1 ± 5
Secondary settling tank	Liquor from carousel reactor	0 ± 1	Effluent	0 ± 0	
			Secondary sludge	2 ± 1	
	Total	0 ± 1	Total	2 ± 1	1 ± 1
Belt thickeners	Excess sludge supply	0 ± 0	Thickened sludge to digester	0 ± 0	
			Reject water to primary settling tank	0 ± 0	
			Off-gas	0 ± /	
	Total	0 ± 0	Total	0 ± 0	0 ± 0
	Primary sludge	0 ± 0	Overflow to primary settling tank	0 ± 0	
		Thickened primary sludge	0 ± 0		
	Total	0 ± 0	Total	1 ± 1	1 ± 1
Anaerobic digester	Total sludge supply	0 ± 0	Effluent to buffer tank	0 ± 0	
			Gas to cogeneration	122 ± 28	
	Total	0 ± 0	Total	122 ± 28	122 ± 28
Digested sludge buffer tank	Effluent from digester	0 ± 0	Digested sludge to centrifuges	0 ± 0	
			Off-gas	4 ± 1	
	Total	0 ± 0	Total	5 ± 1	4 ± 1
Centrifuges	Digested sludge from buffer tank	0 ± 0	Dewatered sludge to storage tank	0 ± 0	
			Reject water to primary settling tank	0 ± 0	
			Off-gas	1 ± 5	
	Total	0 ± 0	Total	0 ± 5	0 ± 0
	Dewatered sludge from storage tank	0 ± 0	Dewatered sludge for incineration	0 ± 0	
		Off-gas	2 ± 1		
	Total	0 ± 0	Total	2 ± 1	2 ± 1
Compost filter	Off-gas to filter	12 ± 4	Gas to carousel reactor	12 ± 3	
	Total	12 ± 4	Total	12 ± 3	0 ± 5
Cogeneration	Biogas from digester	122 ± 28	Methane slip	2 ± 0	
	Additional natural gas from grid	3			
	Total	125 ± 28	Total	2 ± 0	-123 ± 28

$\bar{x} \pm \sigma$ designates mean ± standard deviation.

dewatered sludge content in the storage tank and the emission from the carousel reactor was 0.44.

In order to explain the long-term variation of the methane emission during the measurement period, the possible

correlations between the daily emission and the daily values of a number of relevant process variables were checked (Table 4). The emission from the plug flow reactor was only slightly correlated with the temperature of the mixed liquor (which

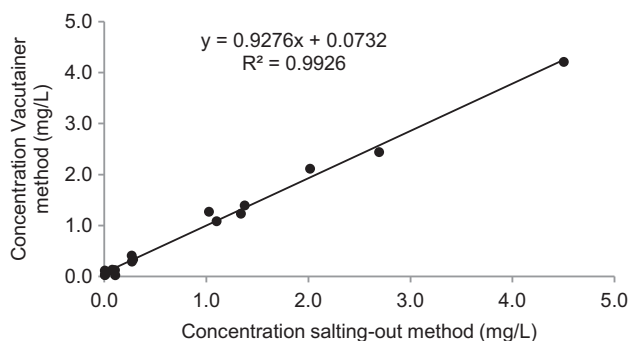


Fig. 2 – Scatter plot of dissolved methane concentrations as determined with the salting-out method and with the vacuum tube method.

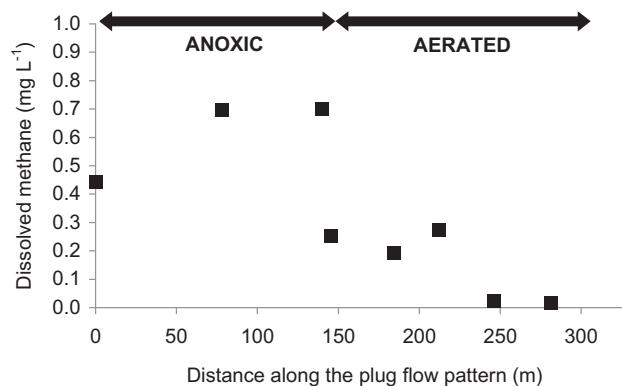


Fig. 3 – Dissolved methane concentration along the path of the plug flow.

ranged from 8.7 to 21.4 °C). For the emission from the carousel reactor and the ventilation system (i.e. after the compost filter), there was only a (weak) correlation with the amount of sludge that was stored in the dewatered sludge storage tank. For the digested sludge buffer tank, data about the stored amount of sludge were not available.

During the monitoring period, the anaerobic digester had an average residence time of 26 days. This may cause a time lag between the effect of the anaerobic digestion related process variables on the actual methane emissions. To suppress the effect of this time lag, the relationships between the emission and the variables related to the anaerobic digestion process on the plant were also verified using the moving averages over 26 days. The results are shown in Table 5. Indeed, the correlations for the moving averages over 26 days turned out higher than the correlations between the daily values. The emission from the carousel and the ventilation system appears to correlate relatively well with the residence time of the sludge in the anaerobic digester, with the amount of sludge that is fed to the dewatering centrifuges and with the amount of sludge stored in the dewatered sludge storage tank.

4. Discussion

4.1. Sampling method for dissolved methane

The validation of the salting-out method by comparing the method with the vacuum tube method yielded very good

results, both in the field and in the laboratory. The salting-out method is accurate, and since the standard deviation of the replicas of the salting-out method was smaller than the standard deviation of the replicas of the vacuum tube method, it is in fact even more precise.

The Vacutainers that were used for the validation were blood serum tubes with a clot activator coating (BD Bioscience #367896) similar to the ones used by Foley et al. (2009) (BD Bioscience #367895). It was found out that empty Vacutainers after equilibrating with the atmosphere already contained about 400 ppm methane. The supplier of the Vacutainer tubes could not give any information regarding the presence of methane. Nonetheless, Genge (1991) showed that coated sterilized Vacutainer tubes (Becton Dickinson) indeed contained up to 248 ppm of methane. According to Genge, the gamma sterilization applied to the tubes cross-links the silicone polymers in the coating. During this process, methane is split out causing contamination. However, uncoated Vacutainer urine collection tubes (BD Bioscience #364915) also contained about 400 ppm of methane. Possibly the methane comes from the rubber septum or the plastic of which the tube itself is made instead of from the coating, but that is irrelevant for the present study.

The salting-out method has some practical advantages over other methods. No toxic compounds are used for stopping the biological consumption or production of methane. In previous studies, this is usually obtained by using inhibiting compounds, such as mercury chloride (Hatamoto et al., 2010; Wang et al., 2011). However, the use of toxic inhibiting compounds may have a harmful effect on the environment and also puts the scientist at risk for harmful exposure to these chemicals. Another way to inhibit biological activity after taking the sample is by filtering the sample before it is brought into the recipient (Foley et al., 2009; Guisasola et al., 2008, 2009), but filtration is only possible for liquids with low solids content, like settled wastewater or treated effluent. On the contrary, the salting-out method can also be applied to slurries like digested sludge or thickened sludge.

4.2. Methane emission compared to carbon dioxide emission

The plant's total methane emission, 2728 ton year⁻¹ expressed as CO₂-equivalents, exceeded the carbon dioxide emission

Table 3 – Results from laboratory validation of salting-out method and vacuum tube method.

Approximate concentration of prepared solution (mg L ⁻¹)	Concentration determined by salting-out method (mg L ⁻¹)	Concentration determined by vacuum tube method (mg L ⁻¹)
	$\bar{x} \pm \sigma$	$\bar{x} \pm \sigma$
0.5	0.51 ± 0.02	0.48 ± 0.05
2.5	2.78 ± 0.09	2.36 ± 0.21

$\bar{x} \pm \sigma$ designates mean ± standard deviation.

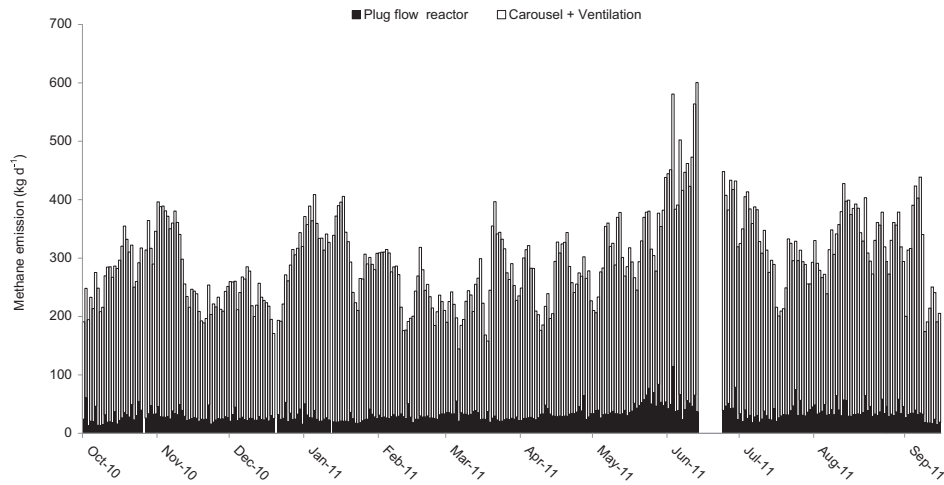


Fig. 4 – Daily methane emission from the plug flow reactor, and from the carousel and the ventilation system.

related to electricity and natural gas consumption ($1500 \text{ ton year}^{-1}$). In the other two Dutch plants, the methane emission was far lower than the carbon dioxide emission (STOWA, 2010). In the Kortenoord plant, the methane emission amounted to $960 \text{ ton CO}_2\text{-equivalents year}^{-1}$, while carbon dioxide was emitted at a rate of $5820 \text{ ton year}^{-1}$. In Papendrecht, the methane emission was $730 \text{ ton CO}_2\text{-equivalents year}^{-1}$ and the carbon dioxide was $3458 \text{ ton year}^{-1}$. Since the normalized methane emissions from the three Dutch plants did not differ that much from each other in comparison with the emission from the Jinan and the Durham plants (Table 1), the higher emission of carbon dioxide from Papendrecht and Kortenoord compared to those plants' methane emission was due to their higher indirect carbon dioxide emission. Kortenoord and Papendrecht emitted about 0.41 and $0.46 \text{ kg CO}_2 \text{ m}^3 \text{ wastewater}$, respectively, while Kralingseveer emitted only $0.05 \text{ kg CO}_2 \text{ m}^3 \text{ wastewater}$. This difference was due to the presence of the anaerobic digester at Kralingseveer. It produced enough biogas to provide about 60% of the plants energy requirements, while Kortenoord and Papendrecht took all required energy from the gas and power grid.

For the Durham and Jinan plants, the ratio between the methane and the carbon dioxide emission could not be calculated. Wang et al. (2011) did not measure carbon dioxide. Czepiel et al. (1993) only measured methane and the biologically produced carbon dioxide that was emitted from the reactors, but not the carbon dioxide that was produced indirectly as a result of fossil fuel combustion to generate the energy required for the operation of the wastewater treatment plant. Only the latter contributes to increased atmospheric carbon dioxide concentrations.

4.3. Sinks and sources of methane

4.3.1. The headworks

At the Kralingseveer WWTP, quite some methane entered the plant via the incoming wastewater. The amount that was stripped in the headworks was negligible. Most of the methane that was formed in the sewer went through the headworks to the primary settler, to the selector and finally to the plug flow reactor. The total methane emission from these four parts amounted to $31 \pm 16\%$ of the total methane

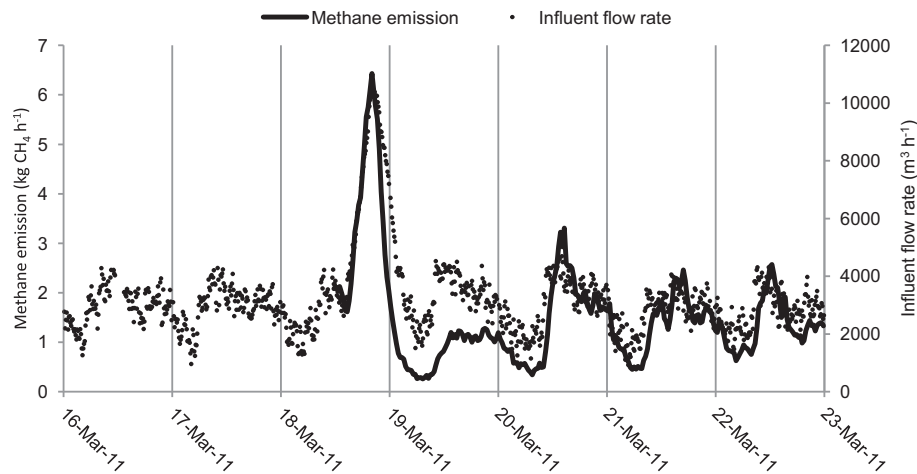


Fig. 5 – On-line methane emission from the plug flow reactor and on-line influent flow rate during one week in March 2011. The vertical gridlines indicate midnight. 18 March 2011 was a wet weather day.

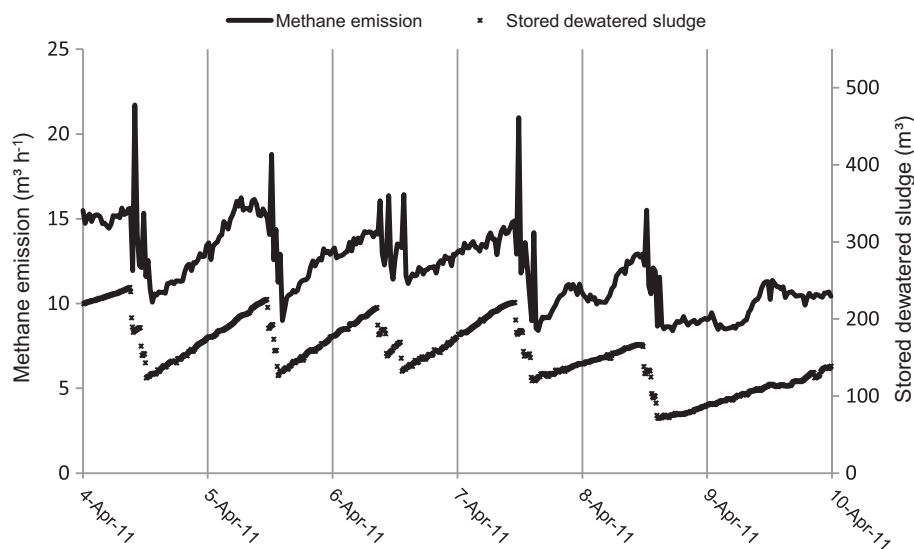


Fig. 6 – On-line methane emission from the carousel reactor and the ventilation system, and on-line volume of the dewatered sludge storage tank content during one week in April 2011. The vertical gridlines indicate midnight.

emission going to the ozone washer (Table 2 and Fig. 1). However, the reject water from the belt thickeners and the centrifuges is returned to the primary settler, together with the overflow water of the primary sludge thickener while the return sludge is fed to the selector and the plug flow reactor. These streams also contain some methane, of which a part can be emitted from the primary settler, the selector and the plug flow reactor. This implies that the methane in the influent contributed certainly less than $31 \pm 16\%$ to the total methane emission from the plant.

The amount of methane that was dissolved in the influent was not measured by Czepiel et al. (1993) nor by STOWA (2010)

nor by Wang et al. (2011). However, for Papendrecht and Kortenoord (STOWA, 2010) 86% and 77% respectively, of the overall methane emission could be traced back to the influent. This could be concluded from the emissions from the headworks and the aeration tank. Due to the short residence time in the headworks, it was unlikely that the methane was formed there. Rather, it was produced in the pressurized sewer mains and stripped in the headworks. This also holds for the methane emission from the aeration tanks. From the profile of dissolved methane depicted in Fig. 3 one could conclude that methane is produced in the anoxic part of the plug flow. However, it is likely that the increase in dissolved methane between the start of the plug flow reactor and 80 m further along the plug flow is a sampling artifact due to the configuration of the plug flow reactor. At the start of the plug flow reactor, the mixed liquor entering the tank from the selector tank is mixed with the recycle mixed liquor coming from the end of the plug flow reactor. Since the second part of the plug flow reactor is aerated, the latter stream does not contain any methane anymore, as can be seen on Fig. 3. Due to non-ideal mixing, it is possible that some of the samples that were taken at the beginning of the plug flow did contain the recycle liquor coming from the aerated part of the plug flow. This explains why the average methane concentration at the beginning of the plug flow is lower than 80 m further along the plug flow. Actual production of methane in aeration tanks is highly improbable because of the anoxic or aerobic conditions in such tanks. So, instead of being produced in the aeration tanks, the methane that was emitted from the Papendrecht and Kortenoord WWTPs must have been produced in the sewer and the part that was not stripped in the headworks was subsequently stripped when it entered the aeration tank. For the Jinan plant, the reported methane emission coming from the influent pump station and the aerated grit chamber, which amounts to the methane from the influent that is stripped upon entering the plant, was only 7–12% of the plant's total methane emission (Wang et al., 2011). For the

Table 4 – Determination coefficient (R^2) between daily mean values of emission and relevant process variables. All determination coefficients were found significant at an alpha level of 0.05.

	Daily emission from the plug flow reactor ($\text{kg CH}_4 \text{ h}^{-1}$)
Influent flow rate ($\text{m}^3 \text{ d}^{-1}$)	0.03
Mixed liquor temperature ($^\circ\text{C}$)	0.17
	Daily emission from the carousel reactor and the ventilation system ($\text{kg CH}_4 \text{ h}^{-1}$)
Atmospheric temperature ($^\circ\text{C}$)	0.08
Biogas production ($\text{m}^3 \text{ d}^{-1}$)	0.00
Residence time of the anaerobic digester (d)	0.08
Sludge supply to the centrifuges ($\text{m}^3 \text{ d}^{-1}$)	0.15
Amount of sludge stored in the dewatered sludge storage tank (m^3)	0.58

Table 5 – Determination coefficient (R^2) between 26 day moving averages of emission and relevant process variables. All determination coefficients were found significant at an alpha level of 0.05.

	Emission from the carousel reactor and the ventilation system (kg CH ₄ h ⁻¹)
Atmospheric temperature (°C)	0.14
Biogas production (m ³ d ⁻¹)	0.11
Residence time of the anaerobic digester (d)	0.84
Sludge supply to the centrifuges (m ³ d ⁻¹)	0.72
Amount of sludge stored in the dewatered sludge storage tank (m ³)	0.70

Durham plant, the methane emission at the entrance of the plant was not reported (Czepiel et al., 1993).

When the part of the emission that can be traced back to the methane coming in with the influent is normalized with incoming COD, this part of the emission amounts to 0.0035, 0.0046 and 0.0067 kg CH₄ (kg COD_{influent})⁻¹ for the plants of Kralingseveer, Kortenoord and Papendrecht, respectively. A possible explanation for the higher value of Papendrecht is the way in which the raw wastewater enters the WWTP. At Kralingseveer and Kortenoord, the raw wastewater is pumped up by centrifugal pumps, while at Papendrecht, the wastewater is pumped up by screw conveyors. In the latter, there is intense contact between the wastewater and the air, leading to a higher stripping rate of methane. This should be taken into consideration when designing new wastewater treatment plants.

4.3.2. Sludge storage

From the mass balances, it is evident that sludge storage contributes significantly to the methane emissions. Methane is produced both in the digested sludge buffer tank, as well as in the dewatered sludge storage tank.

The digested sludge has a considerable residual methane potential because the conversion of the influent sludge to biogas in a completely mixed anaerobic digester is never complete. For instance when a retention time of 20 days is applied in a digester, 5% of the fresh incoming sludge is directly discharged from the system again. Consequently, during digested sludge storage a significant amount of methane can still be produced. The buffer tank for the digested sludge can actually be considered as a second completely mixed digester in series with the two parallel anaerobic sludge digesters, albeit with a residence time of maximum five days and a temperature of about 25 °C instead of 35 °C. The methane production in this tank is about 3 ± 1% of the total methane production in both the anaerobic digester and the buffer tank.

Several studies have been dedicated to additional methane production during digested sludge storage. Hansen et al. (2006) investigated the residual methane that was produced during storage of the effluent of a digester that was used for the anaerobic treatment of municipal organic waste. They

estimated the residual methane potential at 3% of the CH₄ potential of the organic waste treated in biogas plants with a typical retention time of 15 days. Liebetrau et al. (2010) looked into the additional methane that was produced during storage of digestate from a mix of manure and energy crops. In their study, the residual methane potential was on average 5.03% of the total methane production (solid retention time not mentioned). Weiland et al. (2009) obtained an average residual methane potential 3.5% of the total methane production for one-stage biogas installations fed with manure and crops and a solid retention time between 30 and 140 days. So far, the residual methane potential of digested sewage sludge has received no attention, to the authors' best knowledge.

A valorization of the biogas from the digested sludge buffer tank would result in an additional electricity production of about 3 ± 1% and a reduction of 35 ± 13% in the total methane emissions. Normalized by the incoming COD, this would imply a decrease in methane emission of 0.0040 ± 0.0015 kg CH₄ (kg COD_{influent})⁻¹. One way to valorize the residual methane that is produced in the buffer tank is to use the ventilation air from the buffer tank as combustion air in the gas engines of the cogeneration plant. The gas engines use on average 1800 m³ h⁻¹ of air, while the flow rate of the ventilation gas coming from the buffer tank is about 1000 m³ h⁻¹. The remaining 800 m³ h⁻¹ could be taken from the ventilation air from the dewatered sludge storage tank. This stream has the second highest methane concentration, but since its flow rate is 1500 m³ h⁻¹, only part of this stream could be used. The result would be another 1% of additional electricity production and another 15 ± 6% reduction in the total methane emission. Other off-gas streams could be used as well but since their methane concentration is lower, less methane could be recovered. The methane concentration in the ventilation air could of course be increased by using less fresh air for ventilation. This would result in less diluted methane streams, but then the ventilation system should be adapted to handle methane concentrations that exceed the lower explosive limit of methane in air, which is 4.4% (TNO/VNCI, 2008).

4.3.3. Exhaust of the cogeneration plant

The methane slip of the gas engines consists for 98% of methane that was produced in the anaerobic digester, while the remainder comes from the external natural gas that complements the biogas. The methane slip was 1.3%. Although it was based on a single measurement, this value is comparable with other studies that report methane slip from biogas plants. Woess-Gallasch et al. (2010) mention a methane slip of 1.79% as a representative value for Austrian biogas plants. Liebetrau et al. (2010) measured the methane slip of seventeen cogeneration units and obtained an average methane slip of 1.73%.

4.3.4. Primary sludge thickener

Primary sludge contains a lot of readily biodegradable matter. Since the gravitry thickener for the primary sludge has a residence time of about one day, since the conditions are anaerobic and since the primary sludge is inoculated with methanogenic bacteria from the sewer, it is perfectly

understandable that this is a source of methane, be it less than the other sources (Table 2).

4.3.5. Activated sludge as a methane sink

Dissolved methane which enters an activated sludge tank can either be biologically converted to carbon dioxide and water or it can be stripped. Since methane has a global warming potential of 25 CO₂-equivalents, conversion of methane to carbon dioxide leads to a smaller greenhouse gas footprint. Therefore, efforts should be made to promote conversion over stripping. In the case of Kralingseveer WWTP, 80% of the dissolved methane entering the plug flow reactor was converted. If this tank would be a CSTR instead of a plug flow, the dissolved methane in the tank would be more diluted. As a result, the driving force for stripping would be smaller, allowing more methane to stay in solution and to be biologically converted. The methane oxidizing capacity of activated sludge could also be applied for the conversion of gaseous methane, provided that the mass transfer of methane from the gas phase to the liquid phase is enhanced, for instance by using the methane containing off-gases in a bubble aeration system instead of surface aeration.

It has been suggested that methane can act as an electron donor during the denitrification process (Ettwig et al., 2010; Raghoebarsing et al., 2006). That would imply a saving in aeration costs, since no oxygen has to be supplied for the oxidation of methane. However, along the length of the anoxic part of the plug flow reactor, the methane concentration did not decrease (Fig. 3). This indicates that methane is not consumed during the denitrification process. When realizing that already a very significant fraction of the methane is converted aerobically, it is likely that attention to design can further optimize the aerobic methane removal and minimize the emissions.

4.4. The role of anaerobic digestion in the plant's methane emission

While the methane emission of the Kortenoord and the Papendrecht WWTP could be mainly attributed to the methane in the influent, the methane emission from the Kralingseveer WWTP was mainly due to the anaerobic sludge treatment. This also explains this plant's higher emission in comparison with the Jinan and the Durnham plant, both without anaerobic sludge treatment. $72 \pm 23\%$ of the total methane emissions came from the unit processes that are related to the anaerobic digestion facility: the gravitational thickener for the primary sludge, the centrifuge, the buffer tank for the effluent of the digester, the storage tank that contains the dewatered sludge and the methane slip from the gas engines. Therefore, the anaerobic digestion facilities should certainly be taken into account when determining the greenhouse gas footprint of a WWTP.

Because the biogas is used to provide part of the energy requirement of Kralingseveer WWTP, some fossil fuel consumption and its concomitant carbon dioxide emission is avoided. The International Energy Agency (IEA, 2010) estimates the carbon dioxide emission from energy and heat production in the Netherlands at $0.395 \text{ kg CO}_2 \text{ kWh}^{-1}$ (using the typical Dutch mix of energy resources). Based on the

electricity production from biogas in the WWTP's cogeneration unit (13 MWh d^{-1}), the plant's avoided amount of carbon dioxide emission was calculated to be $5.2 \text{ ton CO}_2 \text{ d}^{-1}$. However, the methane emitted by the unit processes related to anaerobic sludge treatment (i.e. the gravitational thickener for the primary sludge, the centrifuge, the buffer tank for the effluent of the digester, the storage tank that contains the dewatered sludge and the methane slip from the gas engines) amounted to $230 \text{ kg CH}_4 \text{ d}^{-1}$. Taking into account that methane has a GWP of 25 CO₂-equivalents (IPCC, 2007), the amount of methane that is emitted from the anaerobic sludge treatment corresponds to an emission of $5.7 \text{ ton CO}_2 \text{ d}^{-1}$. In other words, the methane emitted from the anaerobic digestion facility exceeds the carbon emission that is avoided by valorizing the biogas. Besides, the methane that is emitted to the atmosphere not only contributes to the greenhouse gas footprint of a WWTP, it also implies a waste of energy since the methane emitted from the unit processes that are related to the anaerobic digestion ($7 \pm 2\%$ of the produced methane) could potentially have been used as a fuel for the cogeneration plant.

Although biogas production from waste sludge may be a sustainable technology from an energy point of view, it has in this case no benefits over fossil fuel-derived energy regarding greenhouse gas emissions. Nonetheless it should be emphasized that the emission of methane is not intrinsic for anaerobic digestion, but that a better design and good housekeeping may lead to a drastic mitigation of the emission.

4.5. Dynamic behavior of the methane emissions

4.5.1. Diurnal variability

The diurnal pattern of the emission from the plug flow reactor coincided with the diurnal pattern of the influent flow (Fig. 5). The morning peak of influent flow is closely followed by an increase in methane emission, and on wet weather days, the emission also appeared to be higher than on dry weather days. Despite the similarity between the emission and the influent flow rate patterns, the correlation was not really high ($R^2 = 0.20$). Indeed, Fig. 7 reveals that a low influent rate corresponds with a low methane emission from the plug flow reactor, but at a high influent flow rate, the emission can be both high and low. This can be explained by taking into account the dynamic behavior of the methane emission during periods with a high influent flow rate. Fig. 8 shows the pattern of the methane emission and the influent flow rate during a prolonged wet weather period (characterized by an influent flow rate higher than $6000 \text{ m}^3 \text{ h}^{-1}$). It is clear that the start of a prolonged rain event coincides with a methane emission peak from the plug flow reactor. However, while the influent flow rate remains high for about two days, the methane emission, after showing an initial peak, drops down to a low level after a few hours. This pattern can be explained by considering the presence of biodegradable material in the sewer system. Only if biodegradable material is present in the sewer, methane can be produced. At the beginning of a rain event, a lot of biodegradable material is still present in the sewer and as a consequence, a lot of methane enters the WWTP via the influent, resulting in an emission peak. However, as the rain persists, biodegradable material is

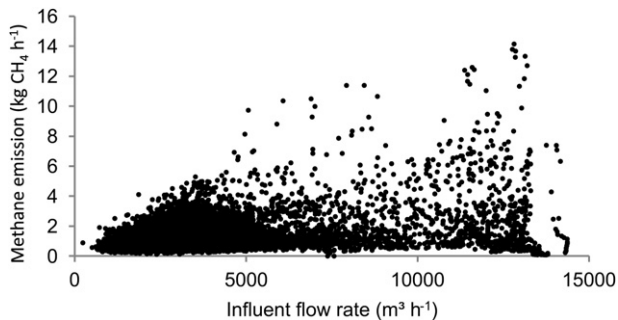


Fig. 7 – Scatter plot of methane emission from the plug flow reactor vs. the influent flow rate.

flushed out of the sewer, leaving relatively clean water in the sewer. The lack of biodegradable material results in less methane being formed in the sewer and less methane that enters the plant. This is reflected in the emission pattern during a prolonged rain event and during a short period after the rain event.

As can be seen in Fig. 6, the short-term emission pattern from the carousel, mainly coming from the off-gas from the ventilation system, is in line with the content of the dewatered sludge storage tank ($R^2 = 0.44$). Every day at about 7 AM, except during the weekend, the dewatered sludge is transferred from the storage tank to a truck. The steady increase in the sludge volume over the day parallels the rising methane emission, while the unloading of the sludge into the truck causes a sharp peak. The correlation is not that strong, but that is because the dewatered sludge storage tank contributes only for $17 \pm 8\%$ to the emission from the carousel reactor.

4.5.2. Seasonal variability

As far as daily values are concerned (Table 4), the only meaningful correlation was between the daily average amount of sludge stored in the dewatered sludge storage tank and the daily emission from the carousel and the ventilation system ($R^2 = 0.58$). Especially considering the limited contribution of the off-gas from the dewatered sludge storage tank

to the emission from the carousel and the ventilation system ($17 \pm 8\%$) this correlation is high. The correlation between the daily values corroborates the correlation between the on-line values.

Regarding the 26 day moving average values (Table 5), a relatively high correlation ($R^2 = 0.70$) was found between the moving average of the emission from the carousel and the moving average of the sludge content in the dewatered sludge storage tank. This was also the case for the on-line measurements and the daily averages, so it is obvious that the amount of sludge that is stored here, influences the emissions. Keeping less sludge in the dewatered sludge storage tank may be an option to decrease this contribution to the total methane emissions.

The 26 day moving average of the emission from the carousel and the ventilation system had a strong negative correlation with the moving average of the residence time in the digester ($R^2 = 0.84$). The amount of sludge that is degraded is inversely proportional to the residence time. The less material that is degraded in the digester, the higher the residual methane potential of the digester effluent will be. Since this effluent is stored in the buffer tank, more methane will be produced there, and since the buffer tank contributes for $40 \pm 15\%$ to the emission from the carousel this emission is influenced by the residence time in the digester.

The digester is operated as a CSTR with fixed volume, which implies that the residence time is determined by the flow rate. The effluent of the digester is first sent to the buffer tank with a maximum residence time of 5 days and subsequently to the dewatering centrifuges. The 26 day moving average of the flow rate to the centrifuges is expected to correlate with the average emission from the carousel, because a higher average flow rate to the centrifuges corresponds with a shorter average residence time in the digester and a concomitant higher residual methane potential. This hypothesis was confirmed by the relatively high correlation that was found between the moving average values of the emission from the carousel on the one hand and the flow rate to the centrifuges on the other hand ($R^2 = 0.72$). As a consequence, increasing the sludge residence time in the anaerobic

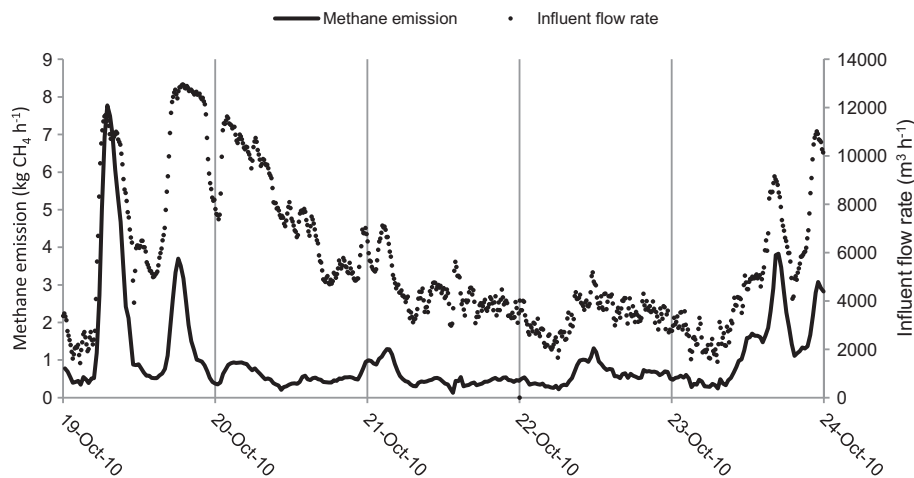


Fig. 8 – On-line methane emission from the plug flow reactor and on-line influent flow rate during a wet weather period. The vertical gridlines indicate midnight.

digester will decrease the residual methane potential and the methane emission during storage of the digester effluent.

5. Conclusions

- The methane emission related to the anaerobic digestion of primary and secondary sludge counts for about three quarters with respect to the WWTPs overall methane emission and causes a slightly larger greenhouse gas footprint than the carbon dioxide emission that is avoided by using the resulting biogas for energy generation.
- Methane emissions can be significantly reduced by better handling of the ventilation air of sludge handling facilities.
- Methane present in the wastewater was for a large part aerobically oxidized in the activated sludge tanks. This could be exploited as a means to further decrease methane emissions from wastewater treatment.
- Dissolved methane can be sampled accurately and precisely with a headspace method based on the salting-out of dissolved gases.

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Appendix A. Supplementary material

Supplementary data related to this article can be found online at [doi:10.1016/j.watres.2012.04.024](https://doi.org/10.1016/j.watres.2012.04.024).

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