CH$_4$ AND N$_2$O EMISSIONS FROM WASTE WATER HANDLING

ABSTRACT

This paper reviews emissions of methane and nitrous oxide from wastewater treatment. For methane, it follows UK experience, relevant to temperate countries with largely centralised sewage treatment, with emissions very heavily dominated by sludge treatment. Sources of methane from sludge processing and disposal or recycling are discussed. Methods for monitoring and estimating methane emissions from sludge treatment are presented. Three methods are given for estimating emissions of methane per country.

Nitrous oxide can be produced both during nitrification and during de-nitrification processes. Its emissions appear to be maximised from both, operating under non-optimal conditions. Though emission factors are tentatively put forward, the uncertainties are very high.

1   INTRODUCTION

This paper highlights issues pertaining to the emission of methane and nitrous oxide from sewage. It was produced as background information for breakout group discussions during the IPCC/OECD/IEA expert meeting, "Good Practice in Inventory Preparations: Emissions from Waste," held 27-29 July, 1999 in Sao Paulo, Brazil. In order to better deal with the topics pertaining to each particular gas, methane and nitrous oxide has been treated separately. This paper focuses on treatment of sewage and sewage sludge. Background information on open sewage and on site treatment systems will be made available at the meeting. The executive summary of the report "Estimates of global greenhouse gas emissions from industrial and domestic wastewater treatment" and "Quantification of methane emissions and discussion of nitrous oxide, and ammonia emissions from septic tanks, latrines, and stagnant, open sewers in the world" is available as an attachment to this paper (Attachment 1 and 2).

2   CH$_4$ EMISSIONS

2.1   Nature, magnitude and distribution of source

Methane is a significant product of the microbially mediated decomposition of a wide range of organic matter in the absence of oxygen, termed anaerobic decomposition. The rates of production of methane can vary enormously - the higher rates requiring a rather precisely engineered set of conditions. The anaerobic digester, used for stabilising sewage sludge, comprises a heated, completely mixed reactor with a retention time measured in weeks. A wide range of fermentative bacteria break down large organic molecules to smaller ones such as fatty acids and alcohols. A much smaller range of more specialised organisms convert these low molecular weight compounds into methane and carbon dioxide. Typically around 40 to 45 percent of the volatile matter in the feed sludge is converted to methane and carbon dioxide. This gas is generally burned to heat the feed sludge to the required operating temperature. At larger sites, the energy balance is usually favourable and allows the gas to be used in a combined heat and power system to generate electricity and heat the feed sludge.

Some leakage and escape of methane is generally unavoidable from such digesters and forms one of the major sources of methane released during sewage treatment. In addition it is common practice, certainly in the UK, to follow such enclosed mesophilic digestion by open, secondary digestion. The amount of methane generated during such secondary digestion is very much lower than during primary digestion, but all of the methane produced from the former escapes to the atmosphere as opposed to only that leaking from primary digesters.

Where conditions are not deliberately engineered, the formation of methane can be very much slower. If, for example, a batch of raw sludge is simply stored, fermentative reactions produce organic acids, causing the pH value of the sludge to drop towards 5. Under such acidic conditions, methane forming bacteria are almost totally suppressed and methane production is extremely slow. Nevertheless, over a timescale of years, which will exist for some methods of ultimate disposal, significant fractions of the sludge are assumed to be converted to methane and carbon dioxide under such conditions.

Very small amounts of methane are released during the processing and short term storage of sludge. Larger releases may occur from the practice of storing sludge in lagoons for long periods - a practice largely discontinued in the UK - but the remaining significant releases come from the ultimate disposal of sludge. Very large amounts of methane will be produced from the disposal of raw sewage sludge to landfill, with smaller but still significant levels produced from the disposal of digested sludge to landfill.

In many countries, a significant fraction of sewage sludge is used in agriculture, to take advantage of its nutrient content (nitrogen and phosphorus). The larger portion of this sewage sludge is believed to degrade aerobically in the soil. In wetter climates, however, it is assumed that soils are waterlogged for a portion of the year and that under waterlogged conditions, some anaerobic decomposition occurs, producing methane.

Disposal of sewage sludge at sea, now phased out in European Union countries, and disposal of untreated sewage to sea, in the process of being phased out for all significant populations, has generally been considered to lead to zero production of methane.

Traces of methane may form in sewer systems. In well graded sewers in temperate climates, this will be insignificant. Some pumped sewers operate totally flooded, thus excluding air, allowing anaerobic conditions to develop. This may lead to the formation of traces of methane. Measurements made on sewer air using a flame ionisation detector can produce a significant response. Such a response however does not differentiate between

methane and other volatile organic carbon and it is likely that the latter dominates. Even if all such response was considered to be from methane, mass emissions are only a few percent of those believed to result from fugitive losses from an anaerobic digester at the same works.

Emissions from primary treatment are believed to be negligible. Measurements on secondary treatment, such as on the air collected from the surface of the activated sludge process, suggests emissions of a similar order to those from sewers. Again, it is likely that non-methane volatile organic compounds (NMVOCs) are dominating these emissions though it is possible some methane is generated within sludge layers held in primary tanks, which is transported in dissolved form into secondary treatment where it is released.

Emissions of methane from sewers and the major sewage treatment processes are probably two orders of magnitude less than from the treatment, storage and disposal of sewage sludge and it is suggested the former are ignored at this time. There may also be emissions from on-site treatment of sewage by individual households in septic systems, usually involving percolation of septic tank overflow into the ground.

The final possible source of methane is from the anaerobic treatment of liquid wastes, as opposed to sludge. Such processes would be impractical if the liquid waste required the same retention time as described above for sludges. This problem is overcome by retaining solids within the treatment process, either in anaerobic filters or anaerobic sludge blanket reactors. The gas from such reactors is retained and burned with emissions of methane resulting mainly from fugitive losses. In temperate climates this process is only applicable to strong and/or warm wastes as they arise in industry. In the UK, which is extensively sewered, the adoption of this process is negligible. In countries which are less extensively sewered, many industries have to treat their own waste and this option is more widely used. Such plants are, however, almost exclusively installed at the industrial premises and it is recommended that such emissions are not included in the sector dealing with sewage.

In warmer climates there is interest in using anaerobic processes, such as described above but also including simple lagoons, for sewage treatment. The resulting methane emissions may need to be considered.

Examples of estimates of methane emissions associated with sewage treatment

UK - Watt (1994) made an estimate of methane emissions from the treatment of sewage sludge. The figure was 69 kt (0.069 Tg) per year. Of this figure 20 kt (0.02 Tg) is emitted from the disposal of sewage sludge to landfill and should already be included in any estimate of emissions from landfill. Hobson and Palfrey (1996) modified this estimate and used it as a baseline to predict future trends, with and without the implementation of measures to reduce emissions. The estimated figure for 1995 was 54 kt (0.054 Tg) per year. The estimated uncertainty in these figures was of the order of 50 percent.

The figures were made up as follows (Table 1):

TABLE 1
BREAKDOWN OF ESTIMATED EMISSIONS OF METHANE FROM SLUDGE TREATMENT, RECYCLING AND DISPOSAL IN THE UK

Process	UK annual estimate emission of methane (Tg)	Comments
Gravity sludge thickening	0.001	
Anaerobic digestion	0.02	Made up from fugitive losses, losses from open secondary digestion, incomplete combustion and failure of combustion plant
Storage in lagoons	0.004	
Use in agriculture	0.008	Comprising the use of both raw and digested sludge
Landfill	0.017	Comprising the use of both raw and digested sludge
Total	0.054	

Since this was produced, measurements have shown that CHP engines operating on biogas can leave a considerable portion of methane unburned. If this proves universal, it could increase the estimate by between 0.01 and 0.02 Tg per year.

In Watt (1994)'s work, the higher figure of 0.069 Tg was rounded up to 0.1 Tg in the final synopsis. This was estimated to be 2 percent of UK methane emissions.

US - Czepiel et al (1993) made measurements of methane emissions from primary (including preliminary) and secondary treatment and worked these up to national annual figures. He then compared them to some theoretical estimates of the total annual national estimates for sewage treatment, as follows (Table 2):

TABLE 2

BREAKDOWN OF ESTIMATED EMISSIONS OF METHANE FROM SLUDGE TREATMENT, RECYCLING AND DISPOSAL IN THE US

Process	US annual estimate emission of methane (Tg)	Comments
Primary treatment	0.0056	Includes preliminary treatment
Secondary treatment	0.0079	
Sludge digestion	0.84	This is the gas produced - no attempt was made to estimate the fraction lost to the atmosphere
Sludge in landfills	0.45	Takes no account of flaring of gas or combustion for energy recovery. Of this figure 70% may be oxidised by methanotrophs.
On-site septic treatment systems	0.044	After allowing for 70% reduction by methanotrophs

This offers confirmation that preliminary, primary and secondary treatment give rise to an insignificant proportion of methane emissions compared to sludge treatment and disposal.

Czepiel estimates 59 million individuals in the US were connected to on-site treatment systems, dominated by septic tanks and soakaways (drainage fields). His estimate makes no attempt to include emissions from these, though it is not clear to what extent septic tank sludges are taken to sewage works.

2.2 Methodological issues

2.2.1 Principles underlying the selection of emission factors

All estimates of methane emissions must be based on measurements of some sort. In the case of sewage treatment however, measurements can be very difficult. This is because most emissions come from fugitive losses from processes or from large area sources - open lagoons, stockpiles of sludge, landfill or fields. Estimates will generally have to be determined by indirect means with very occasional validation where possible.

Methane is generally measured by gas chromatography with flame ionisation detectors (FID) or thermal conductivity detectors, by IR spectroscopy, with or without chromatographic separation and very conveniently by hand-held FID detectors. The latter however does not differentiate between methane and other VOCs.

Partially off-setting the problem of measurement is that methane production from sewage sludge is very heavily studied and well quantified. Two values in particular can be estimated closely.

Amount of methane produced during a typical mesophilic anaerobic digestion process: Sewage sludge dry solids typically contain from 70-80 percent volatile material and from 20-30 percent inert material or ash. In a typical sludge digester, 45 percent of the volatile solids are 'destroyed' - in fact converted to methane and carbon dioxide. It is observed that 1 m^3 of gas, comprising 65 percent methane and 35 percent carbon dioxide is produced for every 1 kg of volatile material converted. This works out as a typical methane production of 143 kg per tonne of dry solids (tds) fed to the digester. (Watt (1994) used 135 kg per tonne of dry solids - the difference is well within the normal operating range). Some portion of this gas will escape to the atmosphere.

A related important figure can also be considered here. Many anaerobic digesters incorporate secondary digestion in open tanks. An estimated 7.5 percent of the volatile solids fed to the secondary digester will be converted in secondary digestion. This amounts to 8 kg methane per tds in the raw sludge. All of this methane escapes to the atmosphere.

Animal Manure: OECD (1991) estimates a potential methane production from animal manures of 200 kg per tds. This equates to the ultimate anaerobic conversion of 65 percent of the volatile material in sewage sludge to CH_4 and CO_2. The residue will be a stable (under anaerobic conditions) humic material. This figure of 200 kg CH_4 per tds from the ultimate conversion of sewage sludge under anaerobic conditions appears very reasonable and was used in Hobson and Palfrey, 1996. (Certain advanced digestion processes claim 70 percent conversion of volatile material - though slightly higher this is taken as support for using the OECD figure).

Two procedures for estimating methane emissions from area sources and from fugitive emissions are worth noting.

(a) The flux chamber: An open bottomed chamber is placed or floated on a solid or liquid surface. Methane-free air is blown into one end of the chamber and collected as it exits from the other end. The methane flux from

the chamber is simply the measured concentration in the exit-air multiplied by the flow-rate of air used. Methane emissions from an entire process or lagoon are estimated by scaling up the emissions from the chamber by the ratio of its area to the area of the whole process.

When the floating version is used on a water surface there is considerable scope for making an over-estimate. If the incoming air impinges on the water surface it can give rise to significant turbulence which may significantly increase the transfer of volatile material into the air. Similarly, if any liquid collects in the tubes leading to or from the flux chamber it can 'reflux' in the air stream and transfer of volatile materials will be greatly increased.

When used on solid surfaces, there is also considerable scope for error. Placing the chamber in position, particularly if care is taken to make a good seal, can cause considerable disturbance of the surface and a greatly increased temporary emission rate of some substances. When a flux chamber is used over a porous material, such as some types of soil, very small pressure differences between the chamber and the soil atmosphere can either greatly increase or greatly reduce the emission rate.

When emission rates are low, it may be possible to use a static chamber and simply monitor the internal rate of increase of methane concentration. The degree of error in flux chamber estimates is unknown.

(b) The micro-meteorological method: Several variants of this procedure exist. In one case, suitable for sources which can be approximated as a point source, a series of methane measurements is made down-wind of the source, at increasing distances, until the concentration cannot be distinguished from the background concentration (that measured just up-wind of the process). It is almost impossible to carry out this procedure meaningfully without using a monitor that provides an instant response to methane. A portable FID detector is suitable, provided it is highly likely that methane is the major volatile organic compound (VOC) being emitted. (The use of an FID with a charcoal disc can greatly reduce the response to non-methane VOCs.)

An atmospheric dispersion model is then used to estimate the emission rate of methane which produces the best match to those measured. Variables to set in the dispersion model include emission rate, wind-speed and direction and atmospheric stability. The latter is estimated from a combination of wind-speed and insolation. It is modified by the presence of buildings and trees and it may be acceptable to select the stability class which produces the closest match to the measured concentrations.

The dispersion model itself is generally considered accurate to within a factor of 2 but there are undoubtedly additional sources of error. Since wind direction varies, it may be acceptable to allow lateral movement to remain within the peak concentration of the plume at any downwind distance. Measurements must, however, be made in a consistent manner since short term peak concentrations of the order of a few seconds can be from 5 to 10 times higher than 10 minute average concentrations.

These two methods for measuring fugitive and area source emissions of methane are given for information. The associated levels of error are, however, not well characterised and the methane emission factors given in the next section are not based, to any significant extent, on these methods of measurement.

2.2.2 Choice of emission factors

There are no routine measurements of methane emissions on which to base estimates of emissions. Occasional measurements have been made via research projects and these along with a knowledge of the processes taking place must be used to make estimates. Three basic methods are proposed in order of increasing complexity. All are based on the annual production of sewage sludge for any country. This will be discussed in more detail in the next section.

Method 1

This method will produce an extremely imprecise estimate but is very simple to perform for any country.

EQUATION 1

Annual methane emissions = Annual sludge production (tonnes per year)

● methane potential (g CH_4 per tonne) ● emission factor

The methane potential is proposed to be 200 kg CH_4 per tonne raw dry solids (rds) based on the OECD figure for animal manures and is equal to the conversion of 65 percent of the volatile solids in sewage sludge to gaseous products.

The emission factor makes an estimate of the fraction of potential methane conversion which takes place and the fraction which reaches the atmosphere without being destroyed. Unfortunately, this factor could vary enormously, from one for a country which relies exclusively on disposing raw sludge at land-fills to zero for a country which disposes of all of its sludge at sea (an option rapidly being prohibited around the world).

Example - UK 1995

Annual sludge production = 1,534,000 tonnes rds per year (CES (1993), Hobson and Palfrey (1996)

Methane potential = 200,000 g/tonne ● 1,534,000 tonnes = 0.307 Tg

Estimated methane release to atmosphere = 0.054 Tg (using method 3)

Emission factor = 0.18

This emission factor may be a reasonable first choice for a country that employs a range of sludge treatment and disposal options and does not rely too heavily on landfill, particularly for raw sludge.

Method 2

This method may be the least satisfactory as it adds significant complexity and may not add too much accuracy.

$$
\begin{array}{|c|}
\hline
\textbf{EQUATION 2} \\
\text{Annual methane emissions =} \\
\sum_i \text{tonnes} \quad \text{rds} \quad \text{processed}_i \bullet \text{methane potential}_i \bullet \text{emission} \quad \text{factor}_i \\
\hline
\end{array}
$$

for each process - *i* - in common use.

Example UK 1995 - Covered anaerobic digesters.

Tonnes rds processed by primary anaerobic digestion = 889 (CES (1993), Hobson and Palfrey (1996).

Methane potential = 200,000 g/tonne ● 889 tonnes = 0.307 Tg

(digester gas produced = 200,000 ● 45/65 ● g/tonne ● 889 tonnes = 0.213 Tg)

Estimated methane release to atmosphere = 0.020 Tg (using method 3, based on 13.5 kg/tonne rds)

Emission factor = 0.065

(fraction of digester gas escaping = 0.094)

The production of biogas in anaerobic digesters comes from the conversion of 45 percent of the volatile material to gaseous products. The methane potential comes from the conversion of 65 percent of the volatile material to gaseous products. The production of methane in a typical anaerobic digester is therefore 45/65 ● 200kg/tonne rds which equals 138 kg/tonne rds. The fraction escaping to the atmosphere is 0.094.

Hobson and Palfrey (1996) estimated methane losses (Table 3) from anaerobic digesters as follows:

TABLE 3		
ESTIMATED LOSSES OF METHANE FROM ANAEROBIC DIGESTERS		
Fugitive losses	**5%**	**from Watt (1994)**
Losses via annular space	3.5%	5% times an estimated 65% of digesters using floating roofs
Venting and incomplete combustion	1.5%	Measurements showing CHP engines to emit unburned methane exceeding 10%, if universal, would increase this significantly.
Total	10%	The micro-meteorological method applied to old floating roofed digesters measured losses of about 13% of the digester gas. (Recent studies performed by WRc)

There are two particular problems when applying Method 2 to disposal routes:

- Figures available may not be based on tonnes raw dry solids e.g. when digested sludge is sent to landfill, and

- Emissions from the disposal routes - landfill and agricultural land - will depend on which processes the sludge has previously been through. Method 3 overcomes this problem.

Method 2 can be made more sophisticated by separately considering raw sludge sent to landfill and digested sludge sent to landfill, similarly for agricultural disposal, in which case it effectively becomes Method 3.

Method 3

The basis of this method is to estimate methane emissions from each treatment and disposal option in common use. The national estimate is as follows:

$$
\begin{array}{c}
\textbf{EQUATION 3} \\
\text{National estimate of methane emissions =} \\
\sum_{i} tonnes \quad rds \quad processed_i \bullet methane\ potential_i \bullet emission \quad factor_i
\end{array}
$$

for each treatment and disposal combination - i - in common use. Methane emissions are separately summed for each step in a treatment and disposal option. Important to this concept is the idea that the methane potential can be progressively used up on passing through a range of treatment and disposal steps. As an example, consider anaerobic digestion followed by disposal to agricultural land. The calculation is as follows:

Primary anaerobic digestion:

Methane emission equals 13.5 kg/ tonne rds (see method 2)

45/65 ● 200 kg per tonne rds of methane potential are used up (138 out of 200 kg per tonne rds)

Secondary anaerobic digestion:

All methane escapes to atmosphere. WATT (1994) estimated that 7.5 percent of the volatile solids leaving secondary digestion are converted to gaseous products. Making a pro-rata comparison with digestion 138 ● 0.075 ● (100 -45)/45 = 12.7 kg CH_4 per tonne of rds escapes from secondary digesters. 12.7 kg per tonne rds of methane potential are used up.

The total methane potential used up in primary and secondary digestion equals 138 plus 12.7 or 150.7 kg per tonne rds. The methane potential left is 49.3 kg per tonne rds.

Disposal on agricultural land:

OECD (1991) estimates that 10 percent of the methane potential is emitted from disposal to land in moist climates. This equals 5 kg per tonne rds. The overall emission of methane by this route is 13.5 +12.7 + 5 = 31.2 kg CH_4 per tonne rds.

This estimate ignores emissions from short term storage which will be very low in these terms. Prolonged storage of periods over several months should be considered as a separate step in a treatment and disposal route.

Table 4, taken from Hobson and Palfrey (1996), provides possible methane emission rates that were developed in the UK, that should allow reasonable estimates of emissions from a range of treatment and disposal routes. Since it was produced, measurements on unburned methane discharged from CHP engines suggest the figure from mesophilic anaerobic digestion may need increasing. Measurements also show that emissions from stored anaerobically digested sludge cake are greater than zero but they are unlikely to be significant.

2.2.3   General comments on the methods for estimating methane emissions

In the not too distant past, it was the policy for smaller anaerobic digesters in the UK to vent to the atmosphere all of their methane surplus to that required for process heating. This would lead to a significant increase in methane emissions above those estimated here. This practice has now almost totally disappeared. In the first case, CHP engines are being increasingly used for energy recovery. This significantly reduces the volume of methane surplus to heating requirements. Secondly, the issue of odour from sewage works is becoming increasingly significant and the deliberate venting of unburned biogas is very undesirable from this viewpoint. Finally, utilities are generally acting in an increasingly environmentally responsible manner.

Nearly all new anaerobic digesters in the UK are of the fixed roof variety with separate gas holders. The percentage of digesters with floating roofs and the associated emissions from the annular space is diminishing.

Care must be taken when preparing national inventories that emissions are not double counted as would be likely to happen if the emissions from sewage sludge sent to landfill were included under emissions from sewage treatment. Emissions from agricultural land may fall into the same category. Nevertheless, it is valuable to make a complete inventory for each sector so that measures to limit emissions can be considered.

TABLE 4		
POSSIBLE EMISSION FACTORS FOR USE WITH METHOD 3		

Unit Process or Disposal Route	Estimated Methane Emission		Reference
	Specific Mass (kg/tonne rds)	**Proportion of Mesophilic Digestion (%)(see note)**	
SEWAGE TREATMENT			
Sewer inlet	0.3	0.2	Czepiel, 1993
Sewage screening	0.3	0.2	Czepiel, 1993
Grit removal	0.3	0.2	Czepiel, 1993
Primary sedimentation	0	0	Czepiel, 1993
Bacterial filter beds	0.3	0.2	Czepiel, 1993
Activated sludge process	0.3	0.2	Czepiel, 1993
Final settlement	0	0	Czepiel, 1993
SLUDGE TREATMENT			
Gravity thickening	1	0.7	WRc
Temporary storage for liquid raw sludge	1	0.7	WRc
3-month storage for liquid raw sludge	36	25	Watt Committee
Mechanical dewatering of raw sludge	<1	<0.7	WRc
Mesophilic anaerobic digestion	21.5	16	WRc
Mechanical dewatering of mesophilic anaerobically digested sludge	<1	<0.7	WRc
Thermophilic aerobic digestion	0	0	WRc
Composting	0	0	WRc
Lime addition to raw sludge cake	0	0	WRc
Thermal drying of sludge	0	0	WRc
3-month storage of raw sludge cake	0	0	WRc
1-month storage of anaerobically digested sludge cake	0	0	WRc
SLUDGE DISPOSAL			
Landfill - raw sludge	195	144	Watt Committee
Landfill - anaerobically digested sludge	52	39	Watt Committee
Agriculture - raw sludge	20	15	OECD / WRc
Agriculture - anaerobically digested sludge	5	4	OECD / WRc
Agriculture - aerobically digested sludge	5	4	WRc
Agriculture - limed sludge cake	20	15	WRc
Incineration	0	0	Watt Committee
Note: proportion of mesophilic digestion - percentage emitted relative to the theoretical amount expected from conversion of 45% of volatile matter.			

2.2.4   Choice of activity data

A Method 1 estimate requires data on the annual mass of sludge produced for any given country. Most countries with a long history of performing significant levels of sewage treatment are likely to have this data available either from a regulatory authority or from an organisation representing the sewage treatment undertakings.

Care needs to be taken since masses of sludge sent for disposal will not be the same as those produced, reflecting the conversion of solids to gas during anaerobic decomposition.

If this data is lacking it can be estimated from figures of the population connected to sewers leading to sewage treatment and a per capita sludge production. A figure of 80g of sludge dry solids per head per day is suggested.

An industrial contribution to sludge production could be estimated separately. The Revised 1996 IPCC Guidelines for National Greenhouse Gas Inventories (*IPCC Guidelines*) recommend separately estimating the discharge of BOD from major industries. This could be used to estimate a sludge production figure. Alternatively, national data may include the population equivalent connected to sewage treatment. This could be used together with a figure of per capita sludge production. This will introduce an extra level of error since the definition of population equivalent for an industrial discharge will often be based on the volume only and may not take into account differences in strength from domestic sewage.

A Method 2 estimate requires data on the masses of sewage sludge passing through the commonly used treatment processes and being sent via the common disposal routes. National statistics should be available for this for those countries with well established sewage treatment facilities.

A method 3 estimate requires data on the mass of sewage sludge passing through each treatment and disposal combination. It is unlikely that this data will be readily available. A knowledge of the industry combined with discussions with a sample of the major utility operators should allow a sufficiently accurate set of data for a method 3 estimate to be prepared from the data for method 2.

2.2.5   Emissions avoided

The majority of methane produced by anaerobic digesters is either burned to heat the feed sludge or in flare stacks. In the UK, all of the larger digestion sites employ CHP engines and this is highly desirable from an engineering viewpoint. Watt (1994) estimated that 85 percent of digester gas in the UK is burned in CHP engines. Whether this is considered as emissions avoided raises difficult questions which can only be answered properly by considering the subsequent disposal routes.

Where the majority of sewage sludge is to be sent to landfill without methane recovery, then anaerobic digestion with combustion of the methane produced (with or without electricity generation) will lead to a very considerable reduction in overall methane emissions. If sludge is to be incinerated, with zero methane generation, then the fugitive emissions from anaerobic digestion represent an overall increase in methane generation. Hobson and Palfrey (1996) estimated that overall the use of anaerobic digestion was about neutral in terms of methane emissions. They also predicted a gradual conversion of floating roofed digesters to those with fixed roofs which would lead to a gradual reduction in emissions - methane is burned which would otherwise escape, this is a genuine emission avoided. Methane recovery at landfills will be a genuine emission avoided but this will be considered when dealing with that sector.

2.2.6   Input to uncertainty expert meeting

Activity data: National data on sludge production or populations connected to sewer does not usually contain a related estimate of uncertainty but in industrialised countries this should be accurate to within 20 percent.

Similarly the estimate of 200 kg CH_4 per tonne raw dry solids for the methane potential of sewage sludge should be accurate to within 10 percent. This is equivalent to an ultimate conversion to gaseous products of between 60 and 70 percent of the volatile material in sewage sludge.

Generally, there will be a much greater uncertainty in the emission factors but this will depend on the treatment and disposal route selected. Emissions from sewage sludge in landfill - assuming there is a steady state established - will only have one major uncertainty, the degree of oxidation by methanotrophic bacteria.

Estimates of 5 percent fugitive losses from digesters plus 5 percent from the annular space of floating roofed digesters are probably accurate to within 50 percent.

The original estimate of 1 percent. unburned methane passing through CHP engines has been discovered to be low by a factor of 10 when measured at 2 sites (WRc unpublished). This could double the estimate of methane losses associated with anaerobic digestion. Liquid fuels are injected into engines following the turbocharger

while gaseous fuels are injected prior to the turbocharger. Leakage at the turbocharger passes directly into the exhaust and appears to be the main candidate for the levels of unburnt methane observed.

CH_4 released from open secondary digesters should be accurate to better than 50 percent.

The uncertainty associated with the OECD estimate that 10 percent of the methane potential is emitted from the application of sludges to land in moist climates is not known by the author but must be high.

With the exception of the level of unburned methane emitted by CHP engines, estimates should be accurate to within 50 percent. Uncertainty in this parameter could increase overall emissions by 100 percent.

2.2.7   Completeness

These estimates of UK methane emissions from sewage treatment have ignored emissions coming directly from on-site treatment. Most of the sludge from on-site treatment is however collected and transported to sewage treatment works and is included in the national statistics for sludge production.

These estimates ignore any emissions coming from the anaerobic treatment of liquid wastes. In the UK, this process is used exclusively for high strength industrial wastes only and occurs exclusively on industrial premises, not at sewage treatment works.

Emissions from sewers, preliminary, primary and secondary treatment of sewage have been shown to be insignificant - in the UK context.

3   NITROUS OXIDE

3.1   Nature, magnitude and distribution of source

During sewage treatment, carbonaceous matter, commonly characterised by its biochemical oxygen demand, BOD, is oxidised to carbon dioxide and water. The process can be designed, by reducing the load on the plant, to also oxidise ammonia to nitrate. In a further modification to the process, a portion typically 50 percent or 66 percent of the nitrate can be de-nitrified in a reaction involving the simultaneous oxidation of carbonaceous matter. This is doubly beneficial as it reduces the load of nutrient reaching the environment and recovers a significant portion of the energy expended in oxidising the ammonia.

Engineers design de-nitrification zones on the basis that the product of de-nitrification is nitrogen gas. It has long been known that under certain conditions such as exist in soils, one of the products of de-nitrification is nitrous oxide. It also appears that nitrous oxide is a by-product of the biochemical oxidation of ammonia to nitrate. The latter is generally considered to occur in two steps. In the first step, performed by nitromonas bacteria, ammonia is oxidised to nitrite. In the second step, performed by nitrobacter, nitrite is oxidised to nitrate. Nitrous oxide emissions are likely to be associated with the first step and may be maximised if the system is under pressure. Krauth K (1993) suggested that nitrous oxide emissions associated with nitrification were associated with conditions of low dissolved oxygen where a portion of the intermediate nitrite took place in the de-nitrification reaction.

It appears then that de-nitrification under strongly reducing conditions, characterised by effectively zero dissolved oxygen leads to predominantly gaseous nitrogen, whereas denitrification in the presence of low concentrations of dissolved oxygen is more likely to lead to the formation of nitrous oxide. Nitrous oxide emissions associated with nitrification would seem to be associated with nitrification under less than optimal levels of dissolved oxygen where simultaneous denitrification also occurs.

Wherever the nitrous oxide is originally generated, emissions will be promoted by turbulent conditions which promote mass transfer. Nitrous oxide generated within an anoxic zone of an activated sludge plant will most probably be emitted from the subsequent aeration zone.

Existing estimates of emissions have been made in the US and in Germany.

Germany

A number of estimates of emissions have been made. Wicht (1995) estimated an annual emission of nitrous oxide from sewage works of 3500 tonnes/year. Schon et al (1994) made an estimate of 20 to 7000 ml nitrous oxide per kg of sludge solids per hour (approximately 40 to 14,000 mg). If applied to an activated sludge plant, the upper figure is an enormous rate and significantly exceeds the N load on conventional plant. Some estimates give nitrous oxide emissions between 685 and $4,000 \mu g/m^2$.h for different types of plants.

USA

Czepiel et al (1993) estimated nitrous oxide emissions from aeration tanks from 0.12 to 1.8 g/m^2.day. This was worked up to 3.2g per person per year which, if a connected population of approximately 200 million is assumed, equals 640 tonnes per year, probably around 10 percent of the estimate for Germany on a per capita basis. The US figures are based on a single site which may not have included any denitrification.

UK

The only UK figures, not published, are based on recent work by WRc. Measured emissions of 960 to 3200 mg per m^3 of sewage treated, from nitrifying activated sludge plants are given. The higher figure follows from a denitrification zone. This equates to 70 to 230 g nitrous oxide per person per year. The lower figure would be similar to that estimated by Wicht. On reviewing the methodology used, however, it turns out that there would have been interference from carbon dioxide at the high levels that occur in the off-gas from respiring systems, so these figures only really represent upper figures.

3.2   Methodological issues

A Tier 1 estimate of emissions for a country could be:

> **EQUATION 4**
>
> Emissions = Annual volume of wastewater treated ● N_2O emitted per m^3

or

> **EQUATION 5**
>
> Emissions = Total population ● N_2O emitted per person per year.

A Tier 2 estimate could be:

> **EQUATION 6**
>
> Emissions = Total area of activated sludge plant ● N_2O emitted per m^2 per year

A Tier 3 estimate could be:

> **EQUATION 7**
>
> Emissions = $\sum_i$ Total area of type i ● N_2O emitted per m^2 per year for type i

Type *i* could be anoxic zones, nitrifying activated sludge, nitrifying activated sludge following an anoxic zone. Other treatment types could specifically include the area of plant with dissolved oxygen levels in the region of 1 mg/l from which nitrous oxide emissions seem to be maximised.

Choice of emission factors

Tier 1: the emission factor might be between 3 and 60 g N_2O per person per year.

Tiers 2 and 3: it is difficult to interpret the existing data with any degree of certainty.

Choice of activity data

Tier 1: This is simply the population connected via sewer to sewage treatment as available from national statistics.

Tiers 2 and 3: The relevant areas would probably need to be estimated from the connected population and the associated load, together with data on the proportion of nitrifying plants and the proportion of de-nitrifying plants and knowledge of typical design parameters.

3.3   Nitrous oxide from land

It has been estimated (Mosier, 1993) that 1 percent of the nitrogen applied to agricultural land is emitted as nitrous oxide via denitrification in the soil (IPCC recommended figure). For the UK the following estimates (Table 5) can be made:

	Digested liquid sludge	Digested sludge cake	Raw sludge	grand total
TABLE 5 **AN ESTIMATE OF THE NITROGEN APPLIED TO LAND VIA SEWAGE SLUDGE IN THE UK**				
	Digested liquid sludge	**Digested sludge cake**	**Raw sludge**	**grand total**
	million tonnes dry solids per year			million tonnes per year
	0.14	0.14	0.28	
nitrogen in solids @ 5%	0.007	0.007	0.014	
nitrogen in liquid at 3% ds and 1500 mg/l	0.007			
Total N applied to land	0.014	0.007	0.014	0.035

If 1 percent is emitted this equals 350 tonnes nitrogen or 550 tonnes N_2O per year. The figure for Germany on a per capita basis would be approximately 1000 tonnes per year to compare against the estimate of 3500 tonnes from sewage treatment.

Choice of emission factor

1 percent of the nitrogen content of sewage sludge applied to land is emitted as nitrous oxide.

A typical nitrogen content of sludge solids is 5 percent. Liquid digested sludge also contains 1500 mg/l ammonia which makes a contribution similar to that contained in the solids.

Choice of activity data

The mass of solids are applied to land annually as obtained from national statistics. If possible this could be broken down into liquid digested and other forms.

Completeness

Nitrous oxide is also produced in combustion processes associated with sewage treatment - incinerators, boilers and CHP plants.

3.4 Nitrous oxide emissions from rivers

The author has only found one paper covering this issue. A short synopsis is presented. McMahon and Dennehy (1999) investigated the South Platte river in Colorado. This river was heavily enriched both in nitrate from groundwater and ammonia from sewage effluent (9-800 µm) (groundwater in the region contained up to 3450 µm nitrate-N). N_2O emission rates ranged from 90 to 32,600 µg N/m^2.day. For the stretch of river in question overall emissions were 2 to 6 ● 10^7 g/year as N (20 to 60 tonnes per year) depending on the time of year. Considering that 800 km out of over 100,000 km of N enriched rivers was studied, total annual emissions from this source in the US could be very much greater than those estimated by Czepiel from all US sewage treatment works.

Choice of emission factor

90 - 32,600 µg N_2O as N/m^2.day

Choice of activity data

Area of rivers should be available from national statistics. Fractions of rivers are believed to be nitrogen enriched.

4 CONCLUSIONS

The paper puts forward procedures for estimating methane emissions whereby a country should estimate chemical oxygen demand (COD) loads emitted both municipally and from a small number of major industries, the proportion of that COD which degrades anaerobically and the appropriate emission factors.

It is suggested in this paper that in temperate countries virtually all COD from soluble COD and non-settleable particulate COD is degraded aerobically and methane emissions are substantially associated with the collected solids or sludge. In such countries *Good Practice* will guide one down a route which predominantly considers the emissions from the sludge associated with sewage treatment. Emission factors must take into account that

much of the methane from sludge treatment processes is collected and burnt. Methane emissions may still be associated with on-site treatment of industrial wastes.

In countries with hotter climates, anaerobic processes are more likely to be employed to treat soluble and non-settleable particulate COD, even from municipal sewage. These must then be given due consideration.

The *Good Practice* procedure may be difficult to follow for countries with little centralised sewage treatment. An approximate or check method was proposed whereby an estimate was made of all of the COD discharged into water-courses, on a simple per-capita basis if necessary. It was then assumed that all settleable COD would degrade anaerobically while non-settleable and soluble COD would degrade aerobically. Suitable emission factors were proposed.

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Attachment 1 Executive Summary of Paper on Greenhouse Gas Emissions from Industrial and Domestic Water Treatment

ABSTRACT

Doorn, M.R.J., R. Strait, W. Barnard, and B. Eklund. *Estimate of Global Greenhouse Gas Emissions from Industrial and Domestic Wastewater Treatment.* Final Report prepared for US EPA, APPCD, Research Triangle Park, NC. EPA-600/R-97-091, September, 1997.

To improve global estimates of greenhouse gas (GHG) emissions from wastewater treatment (WWT), EPA's Air Pollution Prevention and Control Division (APPCD) initiated a field test program to develop GHG emission factors based on actual emissions measurements and to improve country-specific activity data for industrial and domestic WWT. The field test programme involved the use of the open path monitoring/transect method (OPM/TM) technique with Fourier Transform Infrared (FTIR) spectroscopy to measure emissions from two meat processing plants, one chicken processing plant, and two facultative domestic WWT lagoons. In conjunction with the field test programme, research was undertaken to improve the quality of the country-specific activity data that included a search of the most recent literature and interviews with U.S. and European wastewater experts.

This report summarizes the findings of the field tests and provides emission factors for methane (CH_4) and nitrous oxide (N_2O) from WWT. Also, the report includes country-specific activity data on industrial and domestic WWT which were used to develop country-specific emission estimates for CH_4 and N_2O. The report concludes that WWT is unlikely to be a significant source of volatile organic carbon and carbon dioxide emissions.

Global CH_4 emissions from industrial wastewater treatment are estimated to be between 0.6 and 6.1 Tg/yr with a mean value of 2.4 Tg/yr. The biggest contributor to industrial CH_4 emissions from WWT is the pulp and paper industry in developing and Eastern European countries. The second principal contributor to CH_4 emissions from WWT is the meat and poultry industry. Global CH_4 emissions from domestic WWT are estimated to be between 0.6 and 2.1 Tg/yr with a mean value of 1.3 Tg/yr. Russia is believed to be the largest contributor. CH_4 emissions from untreated domestic wastewater may be many times higher than those of treated wastewater.

The report provides rough estimates for global N_2O emissions from WWT. Global emissions from anaerobic domestic WWT are estimated to be 0.5 Tg/yr and wastewater from the meat and poultry processing industries is expected to emit about 0.24 Tg/yr.

For both industrial and domestic wastewater, large relative uncertainties are associated with estimating the overall degree of global WWT. Also, the quantification of the fraction of the wastewater that may decompose under anaerobic conditions is uncertain.

Attachment 2 Executive Summary of Paper on Greenhouse Gas Emissions from Septic Tanks, Latrines, and Stagnant and Open Sewers

Quantification of methane emissions and discussion of nitrous oxide, and ammonia emissions from septic tanks, latrines, and stagnant, open sewers in the world.

Michiel Doorn and David Liles, ARCADIS Geraghty & Miller, Research Triangle Park, North Carolina, and Susan Thorneloe, Environmental Protection Agency, Office of Research and Development, Research Triangle Park, North Carolina.

Open sewers and on-site wastewater treatment systems, including latrines and septic sewage tanks around the world may be a significant methane (CH_4) source that has previously received little attention. This EPA study is a follow-up of an earlier study that developed CH_4 and nitrous oxide (N_2O) estimates from treated industrial and domestic wastewater based on field measurements at anaerobic and facultative lagoons. It is estimated that combined global CH_4 emissions from latrines, septic sewage tanks, and stagnant, open sewers are approximately 29 teragram per year (Tg/yr), with lower and upper bound ranges of 14 and 49 Tg/yr. Major uncertainties in the estimates are associated with the degree to which wastewater in developing and eastern European countries is treated in a specific system; the amount of wastewater that is discharged into stagnant, open sewers; and the degree to which anaerobic decomposition takes place in these sewers.

Latrines in rural areas of developing countries such as China and India are believed to be the single most significant source of methane, accounting for approximately 12 Tg/yr. Total emissions from stagnant, open sewers are estimated at 10 Tg/yr. Also reviewed were nitrogen cycle effects in septic tanks and latrines in an effort to assess ammonia (NH_3) and nitrous oxide (N_2O) emissions from these systems. It was concluded that these systems are not likely to contribute any significant quantity of NH_3 and N_2O to the atmosphere.