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ESTIMATES OF GLOBAL GREENHOUSE GAS EMISSIONS FROM INDUSTRIAL AND DOMESTIC WASTEWATER TREATMENT

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Waste Water	Nitrogen Oxide (N2O)	Stationary Sources		07B
Waste Treatment	Paper Industry			05C, 11L
Greenhouse Effect	Poultry Meat		04A	06H
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FOREWORD

The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, EPA's research program is providing data and technical support for solving environmental problems today and building a science knowledge base necessary to manage our ecological resources wisely, understand how pollutants affect our health, and prevent or reduce environmental risks in the future.

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This publication has been produced as part of the Laboratory's strategic long-term research plan. It is published and made available by EPA's Office of Research and Development to assist the user community and to link researchers with their clients.

E. Timothy Oppelt, Director
National Risk Management Research Laboratory

ABSTRACT

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 program 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 program, 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 teragrams per year (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.

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ABBREVIATIONS AND SYMBOLS

APPCD	Air Pollution Prevention and Control Division
BOD_5	Biological oxygen demand (five day)
BOD_U	Biological oxygen demand (ultimate)
COD	Chemical oxygen demand
DAF	Dissolved Air Flotation
DOE	Department of Energy
EPA	Environmental Protection Agency
FTIR	Fourier Transform Infrared (spectroscopy)
GHG	Greenhouse gas
HRT	Hydraulic retention time
OECD	Organization for Economic Cooperation and Development
OPM/TM	Open Path Monitoring/Transect Method
POTW	Publicly owned treatment work
(T)SS	(Total) Suspended solids
UASB	Upflow Anaerobic Sludge Blanket
UNISY	United Nations Industrial Statistical Yearbook
US	United States
WW	Wastewater
WWT	Wastewater treatment
WWTP	Wastewater treatment plant
°C	Degrees Celsius
°F	Degrees Fahrenheit
Gg	Gigagram (10^9 grams)
ha	Hectare
kg	Kilogram
l	Liter
m	Meter
mg	Milligram (10^{-3} gram)
Mg	Megagram (10^6 grams)
mgd	Million gallons per day
Tg	Teragram (10^{12} gram)
vol.%	Percent by volume
yr	Year
CFC	Chlorofluorocarbon
CH_4	Methane
CO	Carbon monoxide
CO_2	Carbon dioxide
HCFC	Hydrochlorofluorocarbon
HFC	Hydrofluorocarbon
H_2S	Hydrogen sulfide
N_2O	Nitrous oxide
$NO_3^{(-)}$	Nitrate
NO_x	Nitrogen oxides

PFCs	Perfluorocarbons
VOCs	Nonmethane volatile organic compounds

EXECUTIVE SUMMARY

Introduction

Over the last few years, knowledge on major greenhouse gas (GHG) sources has greatly increased. This report focusses on improving global estimates of GHG emissions from wastewater treatment (WWT) which is considered one of the larger minor sources. GHGs emitted from WWT include methane (CH_4), carbon dioxide (CO_2), nitrous oxide (N_2O), and certain types of nonmethane volatile organic compounds (VOCs).

To improve global estimates of GHG emissions from 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 program 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 program, 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 CH_4 and 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 VOC and CO_2 emissions. The report also provides background information on WWT systems and discusses the effect of water and ambient air temperature on CH_4 emissions and chemical oxygen demand (COD) removal rates in anaerobic lagoons.

Field Tests

OPM/TM using FTIR spectroscopy was used to determine emission rates. A very large data set was generated, and up to 300 separate valid, 5-minute average emission rate determinations were made at a given site. Typical detection limits were about 0.1 gram per second (g/sec) for most compounds, except for CO_2, which had a minimum detection limit of about 150 g/sec. The high detection limit for CO_2 was due to high background concentrations.

At all three meat processing plants, large amounts of CH_4 were measured downwind of the WWT system. The field tests detected significant N_2O emissions only at the anaerobic chicken processing waste lagoon. No N_2O emissions were detected from the anaerobic waste lagoons at the two beef processing plants or the facultative lagoons at the two POTWs. Surprisingly, no emissions of any GHG were detected from the POTW lagoons. However, it is highly probable that CO_2 was being generated, but the levels were too small to measure given the very high background levels of CO_2 and the measurement variability.

With the help of activity factors provided by the plant operators and from the wastewater analyses, emission factors were developed for each site. An estimate of the uncertainty of the emission factors was developed through standard error propagation methods. The derived emission factors all appear to be reliable to within a factor of two, based on random error in the measurements, and assuming that the sites and samples accurately represent the population of interest.

Emission Factors and Methodology

Average CH_4 emission factors based on theoretical models and on empirical industrial digester data are between 0.11 and 0.25 gram (g)/g COD. The average CH_4 emission factor derived from the field tests is 0.96 g/g COD with a lower range of 0.26 g/g COD. The most likely explanation for the fact that the average APPCD field test emission factors are higher, is that the field test emission rates also account for CH_4 emissions from COD that had been deposited in the sludge during past winters when anaerobic microbial activity was low. For the purpose of developing CH_4 emissions estimates for this report, a CH_4 emission factor of 0.3 ± 0.1 g/g COD was used. This factor reflects the upper end of the range of factors based on theoretical models and empirical digester data, and the lower end of the range of the factors developed from the field test results.

The report uses two separate N_2O emission factors. The first emission factor (0.09 g N_2O/g $COD_{removed}$) is based on the field tests and reflects a completely anaerobic environment. It was used to estimate emissions from domestic sewage, meat, poultry, fish, and dairy processing wastewater that is degrading under anaerobic conditions. The second emission factor [5.1 grams per capita per year (g/capita/yr)] is based on literature studies and pertains to anoxic processes (denitrification) as part of conventional domestic WWT.

The equation below was used to estimate CH_4 emissions from industrial wastewater.

$$CH_4 \text{ emissions} = EF * 10^{-12} * \sum_i \sum_c (P_{ic} * Q_i * COD_i * TA_{ic}) \quad (Tg/yr) \qquad (1)$$

where:
- EF = Emission factor (g CH_4 or g N_2O/g $COD_{removed}$).
- P_{ic} = Industry- and country-specific product output [megagrams per year (Mg/yr)];
- Q_i = Industry-specific wastewater produced per unit of product [cubic meters per megagram (m^3/Mg)];
- COD_i = Organics loading removed, by industry (g/m^3);
- TA_{ic} = Industry- and country-specific fraction of COD in wastewater treated anaerobically;
- Subscript i = An individual industry; and
- Subscript c = An individual country.

Initially, 23 industrial categories were identified as potentially the most significant dischargers of wastewater with high organic COD loading. Country-specific annual industrial product output data for each industrial category (P_{ic}) were obtained from the United Nations, Industrial Statistical Yearbook. Typical wastewater generation rates (Q_i) and representative COD loadings (COD_i) were obtained for each industrial category from various literature sources. Country-specific data for Q_i and COD_i were not available.

TA_{ic} expresses the country or region-specific fraction of wastewater for each industrial category that is treated at the industrial site under anaerobic conditions. Very few literature data were found to determine values for TA_{ic} and these are mainly based on anecdotal information from interviews with wastewater experts. In general, only a small fraction of wastewater is treated, even in several "developed" countries. Except for meat processing plants, industrial WWT is usually aerobic. Nevertheless, anaerobic conditions are expected to exist in certain sections of the plant (i.e., sludge storage) or due to mismanagement (e.g., overloading or underaerating of lagoons).

The methodology that was used to estimate CH_4 emissions from domestic wastewater is represented by:

$$CH_4 \text{ emissions} = EF * 10^{-12} * \sum_c (P_c * COD_c * 365 * TA_c) \quad (Tg/yr) \qquad (2)$$

where:
- EF = Emission factor (g CH_4/g $COD_{removed}$);
- P_c = Country population;
- COD_c = Country-specific per capita COD generation (g/day);
- TA_c = Country-specific fraction of COD treated anaerobically; and
- Subscript c = An individual country.

The methodology uses country-specific per capita COD generation rates (COD_c) which were obtained from various literature sources. The country-specific fraction of COD that is treated anaerobically (TA_c) was again based on anecdotal information. As with industrial WWT, only a small fraction of domestic wastewater is treated. In countries that do have comprehensive WWT, this WWT is likely to be primarily aerobic.

GHG Emission Estimates

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. Although pulp and paper wastewater is typically treated aerobically, it was assumed that 15 percent of the COD in pulp and paper wastewater in developing and Eastern European countries decomposes under anaerobic conditions as a result of poor wastewater management practices. The second principal contributor to CH_4 emissions from WWT is the meat and poultry processing industry.

Earlier estimates for global CH_4 emissions from industrial WWT are significantly higher [i.e., between 26 and 40 Tg/yr (U.S. EPA, 1994)]. The two main reasons that the emissions in this current report are lower are, that iron and steel manufacturing and petroleum refining are excluded as significant categories and that the fraction of wastewater degrading anaerobically is significantly lower for most remaining categories. (In U.S. EPA 1994, it was assumed that between 10 and 15 percent of wastewater degrades anaerobically.)

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. One earlier estimate for global CH_4 emissions from domestic WWT is 2.3 Tg/yr (U.S. EPA, 1994). Russia is believed to be the largest contributor. In many developing countries very little wastewater is treated. Whereas much wastewater may end up "on the ground," very significant amounts of wastewater may also be discharged into open sewers and ditches where it may degrade anaerobically. Consequently, CH_4 emissions from untreated domestic wastewater may be many times higher than those of treated wastewater.

Global N_2O emissions from conventional domestic activated sludge WWT are estimated at 0.004 Tg/yr. Estimated global N_2O emissions from anaerobic domestic WWT are 0.5 Tg/yr. Wastewater from the meat, poultry, fish, and dairy processing industries is expected to contain substantial amounts of bound nitrogen, and global N_2O emissions from this source category are estimated at 0.24 Tg/yr. For the United States, emissions are estimated to be 0.12 Tg/yr. As a comparison, previous U.S. estimates for total N_2O emissions are 0.4 Tg/yr and do not include WWT. These estimates are associated with large uncertainties and are, at best, an indication of the relative significance of this source category.

TABLE ES-1. SUMMARY OF GLOBAL CH_4 AND N_2O ESTIMATES FOR DOMESTIC AND INDUSTRIAL WWT.

GHG	*SOURCE*	*LOWER BOUND (Tg/yr)*	*AVERAGE (Tg/yr)*	*UPPER BOUND (Tg/yr)*	*REMARKS*
CH_4	Industrial WWT	0.6	2.4	6.1	
CH_4	Domestic WWT	0.6	1.3	2.1	
N_2O	Domestic Activated Sludge WWT		0.004		These are rough estimates. No lower and upper bounds are available.
N_2O	Domestic Anaerobic WWT		0.5		
N_2O	Anaerobic WWT at meat, poultry, fish, and dairy processing industries		0.24		

Uncertainties

The specific uncertainties associated with the development of the field test emission factor such as the representativeness of the test sites and suitability of the test procedures are discussed in the field test report (Eklund and LaCosse, 1997). The emission factors express CH_4 and N_2O emissions per mass of $COD_{removed}$ as a surrogate for the amount of available organic carbon or nitrogen in the wastewater. The ratio of COD to actual degradable organic loading varies for different types of wastewater and is a source of uncertainty.

For both industrial and domestic wastewater, large relative uncertainties are associated with quantifying the overall extent of global WWT. Also, the quantification of the fraction of the wastewater that may decompose under anaerobic conditions is uncertain. The estimates for industrial wastewater, furthermore depend on quantification of the wastewater outflow and concentration per unit of product. Q_i and COD_i values depend on the product, the production process, and the efficiency of the process. The type and efficiency of the industrial process are likely to be dependent on plant scale, availability and cost of water, local water and wastewater regulations, and the degree of enforcement. It is expected that errors are associated with the extrapolation of data across industries, even within the same industrial category.

INTRODUCTION AND BACKGROUND

A greenhouse gas (GHG) can generally be defined as any gaseous molecule which absorbs infrared light in the spectral region of 5 to 20 micrometers. Reasonably accurate global balances are needed for targeted GHGs for use with climatic models to estimate long-term global temperature changes. The development of a global balance for any compound includes identification of all major emission sources, estimation of their source strength (i.e., emission rate), and identification of all major reaction mechanisms and sinks, as well as, atmospheric residence times. Now that comprehensive efforts by national and international research centers are well under way to quantify GHG emissions from larger sources, more attention is given to secondary sources, such as treated and untreated wastewater.[1] This report focusses on improving global estimates of GHG emissions from treated wastewater.[2]

Methane is believed to be the most important GHG emitted from wastewater treatment (WWT). It is produced during the anaerobic decomposition of wastewater and wastewater sludge. Other GHGs from WWT are carbon dioxide (CO_2), nitrous oxide (N_2O), and certain types of nonmethane volatile organic compounds (VOCs). VOCs are typically discarded in and with wastewater as liquids and may later be emitted especially if the wastewater undergoes turbulence. Also CO_2 and N_2O are products of the biological degradation of organic matter in the wastewater.

In the United States, the Air Pollution Prevention and Control Division (APPCD),[3] National Risk Management Research Laboratory, Office of Research and Development of the U.S. Environmental Protection Agency (EPA) has conducted a program to develop estimates of GHG emissions from waste sources and to compile information on cost-effective control technologies for GHGs. Waste sources include landfills, livestock waste lagoons, and wastewater. As a first step to assess the relative importance of WWT as a source for CH_4 emissions, APPCD conducted an initial desk study in 1991 - 1992 which was summarized in a Report to Congress (EPA, 1994). The 1991 - 1992 study contained a preliminary estimate for CH_4 from WWT, with emissions from global industrial sources between 26 to 40 teragrams per year (Tg/yr) and from domestic WWT of about 2 Tg/yr. The methodology for estimating CH_4 from industrial WWT is based on world wastewater outflows and industry-specific average biological oxygen demand (BOD) values. The domestic wastewater emissions methodology uses country populations and a constant to

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[1] Wastewater is usually classified as either domestic or industrial. Domestic wastewater is the spent water originating from all aspects of human sanitary water usage, whereas industrial wastewater results from industrial operations, including product handling.

[2] Future research will focus on developing estimates of GHG emissions from untreated wastewater, if funding is available.

[3] Formerly named Air and Energy Engineering Research Laboratory (AEERL).

express BOD discharge per capita per day. Both methodologies employ an assumed CH_4 emission factor of 0.22 gram (g)/g BOD.[4]

In this initial study, APPCD recognized that major data limitations existed for quantifying actual emissions from WWT sources, the fraction of wastewater subject to anaerobic decomposition, and the outflow and composition of industrial wastewater. Therefore, APPCD initiated a field test program to develop GHG emission factors based on actual emissions measurements and to improve county-specific activity data for industrial and domestic WWT. The field test program 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 municipal WWT lagoons. Wastewater and process data were collected during the tests to allow for the development of emission factors. The site-selection criteria, sampling and analysis procedures, and results for the field tests are documented in a separate report (Eklund and LaCosse, 1997).

In addition, 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 European wastewater experts. Summaries of the interviews with these experts are included in Appendix A of this report. The most important findings from this research pertained to the extent to which domestic and industrial wastewater is treated and may be summarized as follows:

- There is only one published source (Lexmond and Zeeman, 1995) which provides estimates of the degree to which wastewater is treated in developing and developed countries.

- In developing countries, as well as in Eastern Europe, only a very small fraction of industrial wastewater is treated. Large, multi-national corporations are more likely to treat their wastewater than local industries. Also, in some Organization for Economic Cooperation and Development (OECD) countries significant fractions of raw wastewater are discharged into rivers and oceans via outfalls.

- In many countries (including developing countries and Eastern European countries), sewer infrastructure may not reach large parts of the population, especially in rural areas. In cities in developing countries, domestic wastewater is often discharged into open sewers or gutters where significant anaerobic decomposition is expected to take place.

- In most countries, it is common to discharge large portions of industrial wastewater into public sewers to be treated at the local municipal WWT plant.

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[4] BOD is considered here to be the amount of BOD that is actually used up during CH_4 formation (i.e., $BOD_{influent} - BOD_{effluent}$). For WWT it is assumed that $BOD_{effluent}$ equals zero.

- Around the world, most domestic and industrial wastewater is treated aerobically. Anaerobic biological treatment is only applied to specific kinds of wastewater (e.g., from meat packing plants). Sometimes domestic and/or industrial wastewater also is treated anaerobically, for instance, in situations with severe space constraints or when aerobic systems are not managed properly.

- Environmental regulations may be in place in some developing countries, but there often is very little or no enforcement to ensure compliance with the regulations.

- There are lagoons in use in Africa, Europe, and America. Space constraints limit the use of lagoons in some countries in Asia.

In this current study, the methodology for estimating CH_4 from industrial wastewater has been significantly improved compared to the methodology in the Report to Congress (U.S. EPA, 1994). The accuracy of CH_4 estimates from industrial and domestic WWT was further improved by using the validated emission factors and the more comprehensive and better activity data set. The new methodology allows for country-specific emission estimates and it includes industrial wastewater that is being discharged into public sewers. The methodology for estimating CH_4 emissions from domestic wastewater was not changed compared to the Report to Congress version, with the exception that, for both methodologies chemical oxygen demand (COD) is used instead of BOD. COD is believed to be a better parameter for measuring organics concentrations than BOD (see below). The improvement of the activity data is founded on better quantitative and qualitative industrial outflow data and on better estimates for the fraction of COD in wastewater that is treated anaerobically.

During the field tests, no emissions of VOCs and CO_2 were detected at any of the sites and N_2O emissions were recorded for only one site. The lack of measurable VOC and CO_2 is believed to be associated with the relatively low emissions of these compounds and constraints on the detection limits of the OPM/TM FTIR sampling technique. Techniques with more sensitive detection limits for VOCs and CO_2 (e.g., flux chamber) would need to be applied to determine the extent to which these compounds are emitted from the lagoons tested. This report includes only rough estimates for total VOCs, CO_2, and N_2O emissions from WWT.

As background information, generic descriptions of an activated sludge treatment[5] plant and a typical lagoon system are given as Appendix B. Also, the report provides the result of a literature study on the effect of water and ambient air temperature on CH_4 emissions and COD removal rates in anaerobic lagoons (Appendix C). The chapter on emissions estimates concludes with an uncertainty analysis and a brief discussion on global WWT trends that may affect GHG emissions. For a more comprehensive discussion on trends that may affect GHG emissions, information on untreated

[5] The term activated sludge treatment pertains to wastewater treatment.

wastewater including septic systems (for example, urban sanitation issues) must be included.

BOD AND COD

BOD and COD are both used as expressions of the mass of organics loadings in liquids such as wastewater in milligrams per liter (mg/l). Because both terms are used extensively throughout this report and other wastewater literature, a short introduction and comparison is warranted.

The BOD test is a batch-type laboratory procedure in which aerobic bacteria are allowed to degrade organic matter in a known liquid sample (e.g., wastewater) for a definite number of days (usually five) at 20°C with excess oxygen in the head space of the closed reactor. The sample may be seeded with bacteria if it is expected that not enough organisms are naturally present in the wastewater. The BOD of the organics originally present in the sample is equal to the amount of oxygen used in the bottle over the test period. A five day period is used almost exclusively in tests throughout the world and the BOD value is denoted as BOD_5. For the purpose of determining GHG emissions from organic matter in wastewater, ultimate BOD (BOD_u) would be a more appropriate parameter than BOD_5, however, the determination of BOD_u takes a long time (infinite, in theory), which makes it an impractical parameter to use. BOD_5 is generally in the range of 60 percent to 70 percent of BOD_u (Metcalf & Eddy, 1991).

COD analysis is a quick test that gives the maximum value for the oxygen that is needed for chemical oxidation of all materials in the wastewater. In the COD test, a wastewater sample is placed in a flask containing chromic acid (dichromate ions and sulfuric acid), a strong oxidizing solution. After heating the sample-oxidant mixture on a burner for 2 hours, the mixture is removed and the amount of dichromate remaining is determined through titration. The amount of dichromate depleted during the test is proportional to the COD of the sample (Metcalf & Eddy, 1991).

Aerobic bacteria use metabolisms that are different from those of anaerobic bacteria. BOD is a measure for the activity of aerobic bacteria and is consequently not well suited for determination of organic carbon loadings in an anaerobic environment. In addition, a 5-day BOD test will not fully degrade all of the biological material (especially proteins and fatty acids) in wastewater. The suspended solids associated with the wastewaters also are biodegradable and their ultimate BOD would not be exerted in the 5 days it takes to run a standard BOD test. Consequently, for CH_4, an emission factor based on COD should be a better predictor of emissions than an emission factor based on BOD.

For wastewaters that contain only readily degradable organics, the BOD_5 is equal to the COD. When the wastewater contains organics that are not readily degradable over a five day period, the BOD_u will be equal to the COD and the BOD_5 will be significantly lower than the COD. Also, if a significant concentration of inorganic compounds, such as metal salts, is present, the COD will be higher because the oxidation of these compounds also requires oxygen. For the purpose of studying GHG emissions from anaerobic wastewater, this fact may not necessarily be of great significance, because wastewater

with high inorganic loadings would likely be treated with physical or chemical methods as compared to biological methods and would, therefore, not be a source of the major GHGs (i.e., CH_4 and N_2O). Table 1 includes empirical COD/BOD_5 ratios for different types of wastewater.

TABLE 1. COD/BOD RATIOS FOR WASTEWATER

INDUSTRY	*COD/BOD_5 Ratio*	*INDUSTRY*	*COD/BOD_5 Ratio*
Beef, Pork, Poultry Slaughtering and Processing[1]	3	Grain Processing, Starch Production[1,2]	1.7 - 2
Dairy Products[1]	2	Fish Processing[1]	1.5
Edible Fat and Oil Processing[1]	1.5	Vegetables, Fruit Processing[1]	1.5
Sugar Refining[1]	1.5	Soft Drinks, Juices Production[1]	2.5
Coffee Processing[1]	3	Alcohol Production[1]	3
Fermentation (Yeast)[2]	2.5	Beer Brewing[1,2]	1.5 - 2.5
Paper, Pulp Production[2]	2	Raw Sewage[3]	2 - 3

[1] From Lexmond and Zeeman (1995) (no ranges provided).
[2] From Paques (1994) (no ranges provided).
[3] From Lettinga, et al. (1983) and Metcalf & Eddy (1991).

FIELD MEASUREMENT OF GHG EMISSION RATES AT FIVE WWT LAGOONS

In 1995, Radian Corporation and E.H. Pechan & Associates under contract with APPCD conducted field tests at five WWT lagoons in the Midwestern, Southwestern, and Southeastern United States. The objective of the tests was to develop emission factors for each target compound. The target compounds of interest included CH_4, CO_2, N_2O, as well as CO, and certain VOCs. The technique used to perform ambient air measurements was an OPM/TM approach with a FTIR spectroscopy instrument. Simultaneously, process data were collected to characterize the influent and effluent wastewater at the field sites.

The field work involved being on site for about five days at each facility. Ambient air measurements were made immediately upwind and downwind of the lagoons. The FTIR light beam was directed along a path of several hundred feet and the absorbance of gases was measured. Emission rates were determined from measurements of the ambient concentrations and the atmospheric dispersion characteristics at the time of sampling. In addition, a limited number of influent and effluent wastewater and sludge samples were collected. The field test results are documented in a separate report (Eklund and LaCosse, 1997).

SITE SELECTION

Site-selection criteria were developed to identify those industries and WWT processes that have the greatest potential for measurable emissions of CH_4 and other GHGs. The site-selection criteria include:

- WWT system is likely to emit CH_4 or other GHGs;
- Facility type is among those treating the largest annual mass of BOD/COD in wastewater;
- WWT at specific site of interest is representative of practices within the industry or is representative of WWT practices in developing countries;
- Influent BOD/COD loadings are relatively high;
- BOD/COD removal primarily occurs in lagoons;
- Site terrain is conducive to Gaussian plume dispersion (reasonably level terrain, few windflow obstructions such as buildings and trees, low berms around the lagoons or low tanks, etc.);
- No or few other significant emission sources in the area;
- Access around the lagoon for easy set-up of sampling equipment;
- Access for collecting influent and effluent samples; and
- A high degree of cooperation from the on-site WWT operators.

Site selection focused on U.S. WWT systems that employ open, anaerobic lagoon processes to achieve high levels of BOD or COD removal. First, industries that treat large volumes of wastewater and remove large amounts of BOD/COD were identified using published information sources. Then, additional information was collected from EPA regulatory personnel, project files, and reports and researches in the WWT field to identify which industries were most likely to treat wastewater to remove high levels of

BOD/COD in open, anaerobic lagoons, and to identify the most promising sites for sampling. The most promising candidates were beef and poultry processing plants and pulp and paper mills. Municipal WWT plants, often referred to as publicly owned treatment works (POTWs), also were of interest because they are used to treat a significant fraction of wastewater both nationally and globally and, also, they were thought to be a potentially significant source of N_2O emissions.

Five sites were selected for testing: two beef processing plants, one chicken processing plant, and two POTWs. Two beef processing plant sites and two POTWs were included to help determine the variability in emissions within a given category. Pre-sampling surveys were conducted at these sites to confirm that they met the site-selection criteria for sampling. All testing took place during summertime conditions.

RESULTS

OPM/TM using FTIR spectroscopy was used to determine emission rates. A very large data set was generated, and up to 300 separate valid, 5-minute average emission rate determinations were made at a given site. The air measurement data were reviewed to identify those compounds found in significantly greater concentrations in the downwind air versus the upwind air at each site. Any such compounds were likely to have been emitted from the lagoons being tested. Many of the target analytes were found at the same concentration levels upwind and downwind of the lagoons (i.e., they had no quantifiable emission rate). Only CH_4 and the SF_6 tracer gas generally were present in greater amounts in the downwind air.

The minimum quantifiable emission rate varied from site to site and from one 5minute period to another. The detection limit for a given compound, in terms of g/sec, is dependent on the smallest difference between downwind and upwind concentrations that could be identified apart from the measurement variability within each of the upwind and downwind data sets. For each increment of 0.5 ppmv (500 ppbv) that a given compound was present in greater concentrations downwind than upwind, its emission rate was about 1 g/sec (depending on the molecular weight of the compound). Typical detection limits were about 0.1 g/sec for most compounds, except for CO_2, which had a minimum detection limit of about 150 g/sec. The high detection limit for CO_2 was due to the high background concentrations (e.g., up to 500 ppmv) and the measurement variability (e.g., % CV = 7.5 percent, or 37.5 ppmv).

At all three meat processing plants, large amounts of CH_4 were measured downwind of the WWT system. For the two beef processing plants, the concentration of CH_4 exhibited an exponential-type relationship with wind speed. The downwind CH_4 concentration at the chicken processing plant did not show a clear relationship between concentration and wind speed. At the chicken processing plant, however, the range of wind speeds was much smaller than for the meat processing plants and the number of valid measurement periods also was much smaller, making it more difficult to identify trends and relationships. There also was a thick grease layer present on top of the lagoon which would tend to diminish the effect of surface winds on air emissions and which may have affected the emission rates in other ways also. For example, the grease layer may

trap certain emissions and release these periodically. The emission rates measured at each site for CH_4 and other selected compounds are given in Table 2.

TABLE 2. MEASURED EMISSION RATES OF SELECTED COMPOUNDS FOR EACH FIELD SITE

SITE	GAS	AVERAGE DOWNWIND CONC.	AVERAGE UPWIND CONC.	MAXIMUM DOWNWIND CONC.	AVERAGE EMISSION RATE
		ppm	ppm	ppm	g/sec
Beef Processing Plant in SW U.S.	CH_4	61.9	2.3	142	280
Beef Processing Plant in Midwest U.S.	CH_4	58.1	2.83	200	230
Chicken Processing Plant in SE U.S.	CH_4	9.80	1.92	29.9	180
	N_2O	563 ppb	542 ppb	586 ppb	2.6
POTW for Small Town in Southwest U.S.[a]	CH_4	2.20	2.14	2.46	<0.15
	CO_2	342	351	384	<150
POTW for Very Small Town in Southwest U.S.[a]	CH_4	2.11	2.16	2.81	<0.15
	CO_2	528	668	691	<150

[a] Methane and carbon dioxide values are shown for the POTWs for comparison purposes. No quantifiable emissions of these compounds were detected at either POTW.

The field tests detected significant N_2O emissions only at the anaerobic chicken processing waste lagoon. No emissions (i.e., ‹ 0.1 g/sec) were detected from the anaerobic waste lagoons at the two beef processing plants or the facultative lagoons at the two POTWs.

Surprisingly, no quantifiable emissions were detected from the POTW lagoons. It was expected that either CH_4 or CO_2 or both would be detected at greater concentrations downwind versus upwind. The dissolved oxygen (DO) level in the lagoons exceeded 2 mg/L, indicating that BOD removal is taking place under aerobic conditions. So it is highly probable that CO_2 is being generated, but the levels were too small to detect given the very high background levels of CO_2 and the measurement variability. In general, anaerobic degradation can be expected to produce a mixture of CH_4 and CO_2 (generally somewhere between a 50:50 and a 70:30 ratio). Therefore, emissions of CO_2 would be expected wherever quantifiable emission rates of CH_4 were found. The lack of quantifiable CO_2 emission rates may be due to the high detection limit for CO_2 emission

rates, as previously discussed. The absence of CO_2 emissions also could be due to the consumption of CO_2 by cyanobacteria (blue-green algae) in the lagoons.

The wastewater data for all three meat processing plants are very similar, with the two beef processing plants showing very good agreement. All three WWT systems have high BOD removal rates (88-95 percent), as well as high removal rates for COD, total organic carbon, and nitrates.

The two POTWs had similar influent wastewater and exhibited similar performance in terms of removal of BOD, COD, and total organic carbon. Both systems generated nitrates as a by-product of biodegradation.

Activity factors were developed for each site based on information provided by the plant operators and from the wastewater data. Emission factors were developed for each site by dividing the average emission rates by the activity factors for each site. The various resulting emission factors are given in Table 3. An estimate of the uncertainty of the emission factors was developed through standard error propagation methods. The derived emission factors all appear to be reliable to within a factor of two, based on random error in the measurements, and assuming that the sites and samples accurately represent the population of interest.

TABLE 3. AVERAGE EMISSION FACTORS FROM FIELD TESTS

COMPOUND	EMISSION FACTOR	AVERAGE	RANGE
Methane	g CH_4/head of cattle	4,200	3,500 - 4,800
	g CH_4/chicken	120	n/a
	g CH_4/kg meat	37	15 - 74
	g CH_4/L of wastewater	2.7	1.6 - 4.6
	g CH_4/g influent BOD	1.5	0.40 - 3.2
	g CH_4/g BOD	1.6	0.43 - 3.4
	g CH_4/g COD	0.96	0.26 - 2.0
Nitrous Oxide	g N_2O/chicken	1.8	N/A
	g N_2O/kg meat	1.1	N/A
	g N_2O/L of wastewater	0.067	N/A
	g N_2O/g BOD	0.051	N/A
	g Total Kjeldahl Nitrogen (TKN)	1.7	N/A

N/A = Not applicable

It is possible that the lagoons are a sink for suspended and colloidal material (i.e., insoluble BOD) and this material builds up over time in the lagoon sediments. If so, the degradation of the sediments may occur during summer months or whenever the sediment

is resuspended, thereby increasing the CH_4 (and CO_2) emissions. However, no seasonal trend is evident in the BOD effluent levels in the long-term wastewater data provided by the plants. A discussion on the theoretical effect of lagoon water temperature on the organics removal rates and GHG emissions is provided in Appendix C of this report.

CONCLUSIONS

Several conclusions can be drawn from the study:

- The OPM/TM FTIR measurement approach used in this study was successful for the simultaneous collection of large amounts of ambient concentration data for CH_4;
- The use of the OPM/TM FTIR technique for estimating emission rates from the lagoons had insufficient sensitivity for certain compounds, such as H_2S and VOCs, due to limitations in the FTIR analysis. For most of the sites, the sensitivity for CO_2 was limited by the high background concentrations and the variability in the background concentrations;
- Anaerobic WWT lagoons are a significant source of CH_4 emissions; and
- Lagoons at POTWs are not a significant source of any GHGs, with the possible exception of CO_2.

ADDITIONAL INFORMATION ON GHG EMISSIONS FROM WWT

METHANE AND CARBON DIOXIDE

This section contains stoichiometric decomposition models that were used to develop theoretical emission factors for CH_4 and CO_2. Four literature sources were found that included data on CH_4 and CO_2 emissions from wastewater and summaries from these studies are included as well.

Stoichiometric Decomposition Models

Theoretical emission factors for CH_4 and CO_2 emissions from wastewater can be calculated using simple, stoichiometric decomposition models that represent ultimate decomposition analysis. Two models are presented, one for anaerobic and one for aerobic environments. The models assume that sludge and bacterial cell mass in the wastewater are steady state and provide two variants as a surrogate for average domestic sewage; glucose ($C_6H_{12}O_6$) and the average stoichiometric composition of new bacterial cell matter, as in fresh sludge (represented by $C_5H_7O_2N$) (Metcalf & Eddy, 1991, p. 379).

The organic matter in domestic wastewater can be divided into three main classes: proteins, carbohydrates, and fats. Proteins make up between 33 and 50 percent and will usually have a carbon content that is somewhat higher than that of glucose, due to their hydrocarbon chains. However, according to Mudrack and Kunst (1986), it is acceptable to represent carbohydrates and fats by glucose.

The theoretical emission factors that are calculated here do not take other competing degradation mechanisms into account. For example, oxygen may also be required for oxidation of nitrogen, phosphorus, or sulphur compounds. Oxygen required for these and other processes will increase COD values. On the other hand, the carbon content of glucose is 40 percent by mass, whereas the carbon content of human feces is higher (40 to 55 percent) (Gloyna, 1971). Due to the higher carbon content, CH_4 production from feces can be expected to be higher than that of an equivalent mass of glucose. The increase in CH_4 generation is offset by the increase in COD to a certain degree. More information is required to assess whether the theoretical emission factor representing real sewage differs from the one for glucose.

Model 1: Anaerobic Process (Complete Reaction)—

Glucose

The anaerobic decomposition of glucose is represented by: $C_6H_{12}O_6 \rightarrow 3\ CO_2 + 3\ CH_4$. One mole of glucose weighs 180 g and produces 3 moles of CH_4, which weigh $3 \times 16 = 48$ g. Therefore, the CH_4 production rate per gram of glucose is $48 \div 180 = 0.27$ g. The oxidation of one mole of glucose requires six moles of oxygen (equal to 192 g), [i.e., the BOD_U, as well as, the COD of one mole of glucose is 192 g ($C_6H_{12}O_6 + 6\ O_2 \rightarrow 6\ CO_2 + 6\ H_2O$)]. Therefore, the COD of one gram of glucose $192 \div 180 = 1.07$ g O_2. Accordingly, one gram of COD correlates with $0.27 \div 1.07 = 0.25$ g of CH_4, which is the emission factor.

As mentioned before, this model assumes that all BOD is degraded over time and the amount of sludge and cell matter is steady state.

The CO_2 emission factor can be calculated in a similar way. Under anaerobic conditions, for every gram of glucose $(3 \times 44) \div 180 = 0.73$ g of CO_2 is produced. Accordingly, the emission factor is $0.73 \div 1.07 = 0.69$ g CO_2 / g BOD.

Average Bacterial Cell Matter

The CH_4 emission factor was also calculated for new bacterial cell matter in wastewater, which may be expressed as $C_5H_7O_2N$ and is used as a surrogate for domestic sewage. The complete anaerobic decomposition of any organic compound containing C, H, O, and N is represented in Equation 3.

$$C_aH_bO_cN_d + [(4a-b-2c+3d)/4]H_2O \rightarrow [(4a+b-2c-3d)/8]CH_4 + [(4a-b+2c+3d)/8]CO_2 + (d)NH_3 \quad (3)$$

For $C_5H_7O_2N$, Equation 3 may be rewritten as:

$$2C_5H_7O_2N + 6H_2O \rightarrow 5CH_4 + 5CO_2 + 2NH_3 \quad (4)$$

One mole of $C_5H_7O_2N$ weighs 113 g (dry) and produces 2½ moles of CH_4 equal to 40 g. Therefore, for every gram of average dry sewage, $40 \div 113 = 0.35$ g of CH_4 is produced.

$$C_5H_7O_2N + 6O_2 \rightarrow 5CO_2 + 2H_2O + NH_3 \quad (5)$$

As Equation 5 indicates, one mole of $C_5H_7O_2N$ requires 6 moles of O_2 equal to 192 g COD, (i.e., the COD of $C_5H_7O_2N$ is $192 \div 113 = 1.70$ g). Thus, for every gram of CH_4 produced, 1.70 g of COD are required and the emission factor thus becomes $0.35 \div 1.70 = 0.21$ g CH_4 per gram of COD.

The CO_2 emission factor can be calculated in a similar way. For every gram of $C_5H_7O_2N$, $(5 \times 44) \div 113 = 1.95$ g of CO_2 is produced. And for every gram of CO_2 produced, 1.70 g of COD is required. Accordingly, the emission factor is $1.95 \div 1.70 = 1.15$ g CO_2 / g COD.

Model 2: Aerobic Process—

Glucose

The aerobic decomposition of glucose is represented by: $C_6H_{12}O_6 + 6\ O_2 \rightarrow 6\ CO_2 + 6\ H_2O$. For every gram of glucose, $264 \div 180 = 1.47$ g of CO_2 is produced. As before, for every gram of glucose, $192 \div 180 = 1.07$ g O_2 (COD) are needed. Accordingly, the emission factor is $1.47 \div 1.07 = 1.38$ g CH_4/ g $COD_{removed}$.

Average Bacterial Cell Matter

The complete aerobic decomposition of any organic compound containing C, H, O, and N is represented in Equation 6.

$$C_aH_bO_cN_d + [(4a+b-2c-3d)/4]O_2 \rightarrow aCO_2 + [(b-3d)/2]H_2O + bNH_3 \quad (6)$$

or, for $C_5H_7O_2N$:

$$C_5H_7O_2N + 5O_2 \rightarrow 5CO_2 + 2H_2O + NH_3 \quad (7)$$

One mole of $C_5H_7O_2N$ weighs 113 g and produces 5 moles of CO_2, which weigh 5 × 44 = 220 g. Therefore, for every gram of average $C_5H_7O_2N$, 220 ÷ 113 = 1.95 g of CO_2 is produced. One mole of $C_5H_7O_2N$ requires 5 moles of O_2 or 160 g. So, for every gram of $C_5H_7O_2N$, 160 ÷ 113 = 1.42 g of O_2 (COD) are needed and the emission factor thus becomes 1.95 ÷ 1.42 = 1.37 g CO_2 / g COD.

Table 4 summarizes the theoretical emission factors that were developed in this chapter. Based on the CH_4 emissions data in Table 4, it becomes apparent that the 0.22 g/g BOD number introduced by Orlich and used in prior reports is likely to have been derived from similar calculations. One other theoretical value was found in the literature; Viraraghavan and Kikkeri (1990) report a theoretical maximum value of 0.3 m^3 CH_4 per kg COD for dairy wastewater at standard temperature and pressure. This converts to 0.21 g/g COD. Note that although "new bacterial cells" have a higher mass percentage of carbon than glucose, the CH_4/g COD emission factor is lower.

TABLE 4. THEORETICAL CH_4 AND CO_2 EMISSION FACTORS

	ANAEROBIC DECOMPOSITION		AEROBIC DECOMPOSITION
	g/g COD or g/g BOD_U		
Sewage composition represented by:	**CH_4**	**CO_2**	**CO_2**
$C_6H_{12}O_6$ (glucose)	0.25	0.69	1.38
$C_5H_7O_2N$ (new bacterial cells in wastewater)	0.21	1.15	1.37
Average	0.23	0.92	1.375

Summaries of Four GHG Wastewater Studies

Only three references were found that describe field tests to measure CO_2 and CH_4 from WWT plants. Also, one manufacturer of anaerobic digester systems provided useful CO_2 and CH_4 data. Pertinent information is summarized below.

Field Test at U.S. Activated Sludge POTW—

Field tests were conducted at an activated sludge POTW in Durham, New Hampshire over a period that ran from mid-winter to summer (Czepiel et al.; 1993.) The average influent concentration at the plant is approximately 250 mg BOD_5/l and the average removal efficiency is 94 percent. Significant amounts of CO_2 were detected and some CH_4 was also measured. Depending on the location in the plant different sampling techniques were used. To take samples from nonaerated surfaces, a closed chamber technique was used, whereas, a bag technique was used for emissions from aerated surfaces. Because the plant is aerated (with the exception of the sludge digestion) it may be that the CH_4 emitted was already present in the sewage and is merely stripped from the liquid. This indicates that anaerobic decomposition must have taken place in the sewer lines.

As the degree of aeration is not specified, the CH_4 emissions may only be extrapolated to similar types of treatment plants. The CH_4 and CO_2 emission rates from Czepiel et al. are given in Table 5. Total BOD_5 related emission factors for CO_2 and CH_4 may be calculated by dividing the total yearly gas emission rates by the average total yearly BOD that is removed. The emission factors for CH_4 and CO_2 are 1.7×10^{-3} g CH_4/g BOD and 1.5 g CO_2/g BOD, respectively.

Czepiel et al. include an estimate of U.S. CH_4 emissions from domestic WWT and anaerobic sludge digestion. They estimate that CH_4 emissions from primary treatment are 6,000 Mg/yr and from aerated sludge treatment, 8,000 Mg/yr (total of 0.014 Tg/yr). The total yield from anaerobic sludge digestion is estimated at 0.84 Tg/yr. If it is assumed that 10 percent of this CH_4 leaks to the atmosphere, the total CH_4 emissions from domestic WWT would be 0.1 Tg/yr or 0.2 to 0.4 percent of total anthropogenic U.S. CH_4 emissions [Total emissions based on U.S. EPA (1994) and U.S. DOE (1994)].

TABLE 5. DATA AND CH_4 AND CO_2 EMISSION RATES FOR POTW IN DURHAM, NH

WWT	RETENTION TIME	INFLOW	CH_4	CO_2	REMARKS
	hrs	l/day	g/yr	g/yr	
Grit removal chamber (aerated)	0.3	$3.0*10^6$ with BOD_5 = 250 mg/L	$0.6*10^5$	$0.4*10^7$	Stripping of gases already present in sewage
Primary settling tank	2.6		$0.9*10^5$	$0.1*10^7$	Possibly some CH_4 generation
Aeration tank	16		$2.2*10^5$	$36*10^7$	Inoculation with sludge, stripping of CH_4; CO_2 generation
Secondary settling tank	10		-----	-----	CH_4 generation is likely, no tests were performed
Sludge holding (partially aerated)	72		$0.6*10^5$	$2.1*10^7$	Stripping of CH_4; CO_2 generation
Total			$4.3*10^5$	$39*10^7$	BOD_5 removal efficiency = 94%

Biogas Measurements at an Anaerobic Lagoon in Portugal—

Toprak (1995) describes a field-study at a WWT plant in Portugal. Domestic wastewater at a community of 30,000 people is treated in a system of lagoons that consists of one anaerobic, three facultative, and one polishing lagoons. The system is designed for 1,200 m^3/day. There are 53 such systems in Portugal and another 40 are under construction, indicating that this type of domestic WWT is suitable for a country such as Portugal. At the anaerobic lagoon, biogas was collected with a small flux chamber and composition and production rates, as well as wastewater characteristics, were recorded over a period of 62 days. From the field test results, Toprak developed a varied range of empirical equations which are included below.

COD removal rates

The mean COD loading rate at the anaerobic lagoon was 0.17 kilogram (kg)/cubic (m^3)/day. This value is lower than the maximum design capacity of 0.42 COD kg/m^3/day. The COD removal efficiency (η) varied between 30 and 68 percent and was dependent on temperature. From the field data, Toprak developed a first-order kinetic model for COD removal. The model is based on the assumption that an anaerobic lagoon is a completely mixed reactor (Equation 8).

$$C = \frac{C_o}{(1 + t * k_{20} * \theta^{T-20})} \quad (8)$$

where: C_0 = influent COD concentration (mg/L);
C = effluent COD concentration (mg/L);
t = mean hydraulic retention time (HRT) (days);
k_{20} = COD removal rate constant at 20°C (0.221 day^{-1});
θ = temperature correction factor (1.117); and
T = water temperature in the pond (°C).

Biogas emissions and composition

Biogas rates varied considerably, depending on influent COD loading rate, and especially on *ambient* air temperature. Biogas consisted predominantly of CH_4, CO_2, and atmospheric N_2. The CH_4 component varied between 50 and 82 percent with a mean value of 71 percent. The lowest value was achieved on days with rain. Apparently, the rain contributes to a significant increase in dissolved oxygen. Weekly averages of biogas emissions and composition and weekly COD removal rates were used to develop emission factors. For CH_4 the mean emission factor was 0.145 m^3/kg COD, which may be converted into 0.10 g CH_4/g COD, using the ideal gas law at 20°C. Toprak remarks that this is 39 percent of the theoretical maximum value and suggests that part of the difference is a result of the conversion of carbon into new cells. Also, the measurement techniques may have contributed to errors and low CH_4 collection rates.

Global CH_4 and CO_2 Emissions for the Food and Beverage, and Pulp and Paper Industries—

Lexmond and Zeeman conducted a study to determine the theoretical maximum global CH_4 and CO_2 emissions for domestic wastewater and wastewater from two industry sectors, the food and beverage industry and the pulp and paper industry. Preliminary findings of their study are summarized in Lexmond and Zeeman (1994), a more detailed report was published in 1995 (Lexmond and Zeeman, 1995). Although the estimates are based on a desk study using pilot scale digester test data, the report is of particular interest because of the well developed methodology and the novel activity data.

Lexmond and Zeeman estimate that wastewater from domestic sources and from the food and beverage and the pulp and paper industries represents over 70 percent of total biodegradable matter present in all industrial wastewater. They further estimate that global CH_4 emissions from wastewater and wastewater sludge are between 5 and 10 Tg/y. Uncontrolled anaerobic digestion of untreated wastewater in developing countries is considered to be the largest source. In their report, Lexmond and Zeeman do not include an estimate of global CO_2 emissions from wastewater.

The paper and report include a methodology which uses the parameters listed in Table 6. This methodology is similar to the one that was adopted in this document. Lexmond and Zeeman conclude that production and utilization of digester gas would offset a significant amount of CO_2, although losses from CH_4 escaping to the atmosphere must be held to a minimum.

TABLE 6. ACTIVITY DATA FOR THE PULP & PAPER AND FOOD & BEVERAGE INDUSTRIES

DESCRIPTION	*UNITS*	*REFERENCES, REMARKS*	*PULP & PAPER*	*FOOD & BEVERAGE*
Annual production	kg/yr or m^3/yr	United Nations, Industrial Statistics Yearbook	Wastewater outflow = $21.2*10^9$ m^3/y	Wastewater outflow = $7.4*10^9$ m^3/y
Wastewater per unit of product	m^3/kg or m^3/m^3	Multiple references		
COD for "fresh" wastewater	g/m^3	Multiple references	2,200	5,600
Fraction treated by certain method	%	Lexmond assumes two cases: 100% aerobic and 100% anaerobic.		
Maximum CH_4 producing capacity	m^3/kg COD	Multiple references	0.026	0.31
COD removal efficiency	%	Assumption	90	90
Biological sludge yield	%	40% for aerobic systems, 10% for anaerobic systems		

Empirical Anaerobic Digester Data—

Paques Environmental Technology, a manufacturer of anaerobic digester systems, has sold and installed hundreds of anaerobic digesters at various industries and municipal WWT plants around the world. Empirical information collected by Paques for the beer, potato, starch, yeast, paper, and wood pulping industries is summarized in Table 7, which includes BOD_5, COD, and biogas production and composition data. These data were used to calculate CH_4 emission factors expressed in g CH_4/g COD and some of the COD/BOD ratios in Table 1 in the Introduction.

TABLE 7. EMPIRICAL WASTEWATER AND BIOGAS DATA FOR SIX INDUSTRIES

INDUSTRY	COD influent	BOD_5	COD removed	BIOGAS PRODUCTION (ANAEROBIC)	BIOGAS COMPOSITION			EMISSION FACTOR[1]
	mg/L x100	mg/L x100	%	m^3/ kg $COD_{removed}$	CH_4 %	CO_2 %	H_2S[2] %	g CH_4 / g $COD_{removed}$
Brewery	15-70	10-45	75-90	0.4-0.45	80-85	15-20	1-2	0.25
Potato Processing	40-160	24-70	70-80	0.45-0.55	45-55	45-55	0.1	0.163
Wheat Starch Production	15-420	9-255	65-85	0.45	70	24	0.5-1.0	0.206
Yeast Wastewater	65-160	30-60	65-70	0.2-0.3	60-70	30-40	1-3	0.106
Paper Production	15-80	7.5-40	75-85	0.45	80	19	1	0.235
Pulping	20-150	10-75	50-65	0.4	75	24	1	0.196

Notes: [1] Based on ideal gas law at 25°C: 1 mole = 24.5 liters.
[2] Hydrogen sulfide.

VOLATILE ORGANIC COMPOUNDS

VOC emissions from municipal WWT plants have received attention because they are a potential health hazard to plant personnel. Also, VOCs are precursors to ground-level ozone formation. Not all VOCs are GHGs. A group of potent GHG/VOCs are the halocarbons, which include:

- Chlorofluorocarbons (CFCs);
- Bromofluorocarbons (halons);
- Hydrochlorofluorocarbons (HCFCs);
- Hydrofluorocarbons (HFCs);
- Perfluorocarbons (PFCs); and
- Other related compounds.

Halocarbons and related compounds are powerful GHGs with, in most cases, very high radiative forcing potentials. CFCs, halons, and some other related compounds are being phased out in 1996, under the Rio Treaty and Montreal Protocol. HCFCs are less stable than CFCs and consequently do not contribute as much to stratospheric ozone depletion. Many HCFCs are toxic and are to be phased out in 2015 under the Clean Air Act Amendments of 1990, as well as, the Montreal Protocol. HFCs have no chlorine and thus have no effect on the ozone layer. This makes them strong, unambiguous GHGs. For instance, HFC-134a, a CFC-replacer used in car air conditioners, has a radiative forcing potential of 4,300 relative to CO_2. PFCs are strong GHGs and are emitted as a by-product from aluminum smelting.

Chlorine containing compounds (including CFCs and HCFCs) tend to react with tropospheric ozone (which is also a GHG) and may, as such be contributing to GHG reduction (sink). The net global warming effect of these gases is unclear at this time.

Unfortunately, no quantitative information was found on GHG/VOCs that are emitted from WWT. Five VOCs that were detected in wastewater air emissions are also known GHGs [US Department of Energy (DOE), 1994], (Table 8). Other VOCs that have been detected in air emissions from WWT may also be GHGs, although little information was available to verify this. The VOCs most commonly found in wastewater (i.e., benzene, toluene, and xylenes) are not known to be GHGs. The ensuing discussion of data found in the literature is geared towards VOC emissions from WWT, regardless of their radiative forcing potential.

TABLE 8. VOC-GHGS DETECTED AT U.S. POTWS

GREENHOUSE GAS	GLOBAL WARMING POTENTIAL (CO_2 = 1)	PRINCIPAL USES
Dichlorodifluoro-methane	8,300	Auto air conditioners, Chillers, Blowing agent
Trichlorofluoro-methane	3,900	Blowing agent, Chillers
Carbon tetrachloride	1,400	CFC feedstock, Solvents
Methylene chloride	10	Solvent
Chloroform	5	HCFC feedstock.

There are many different VOCs found in wastewater. Mihelcic et al. (1993) includes a list of 32 VOCs that have been detected in air emissions at U.S. POTWs that receive domestic and industrial wastewater. Industrial and commercial operations are the predominant source for VOC loadings to POTWs. Predominant chemicals contributed by industry are benzene, toluene, and xylenes; and to a lesser degree, methylene chloride, trichloroethylene, and carbon tetrachloride (chloroform). Benzene, toluene, and xylenes can be associated with petroleum refining operations, whereas, the other VOCs are typically used as strippers and/or industrial solvents. Chloroform may have a potential to be formed during chlorination of drinking water. No information was retrieved on industrial wastewater characteristics and potential VOC emissions for industrial wastewater that is treated on-site. The discussion in this chapter only pertains to VOC emissions from municipal WWT plants.

The three primary VOC removal processes from wastewater are stripping or volatilization, biodegradation, and sorption. In studying air emissions from WWT, stripping is the removal mechanism of principal interest. A significant fraction of VOCs discharged into public sewers may be stripped from the wastewater before it reaches the WWT plant. Quigley and Corsi (1995) measured emissions for total VOCs including benzene, toluene, xylenes, and tetrachlorethene from an interceptor in Toronto, Canada. Measurements included, average emissions of total nonmethane hydrocarbons from a single manhole which amounted to 2.3 Mg/yr. Quigley and Corsi also compared emissions of several VOC species from the interceptor to those from three local POTWs in Toronto, Canada. For all but one species, emissions at the interceptor were higher than at the POTW. Because sewer structures can vary greatly, accurate models for estimating VOC emissions from sewers are difficult to develop. Emissions of VOCs from sewers will depend on the solubility of the VOC species in water, the layout of the sewer, and the degree of ventilation and contact with the atmosphere. At municipal WWT plants, primary treatment processes such as aerated grit chambers, and equalization basins, especially those that require mechanical aeration, are considered to be VOC emission sources.

Many VOCs are also highly biodegradable. Wood et al., (1990) studied the behavior of VOCs at a WWT plant at an organic chemicals manufacturing site and conclude that, "a significant percentage of the pollutant loss across the equalization basin can be accounted for by biodegradation or mechanisms other than volatilization." Hentz et al., (1996) state that at three Philadelphia POTWs over 85 percent (by weight) of 18 targeted VOCs was biodegraded. Generally, in WWT plant environments, nonchlorinated VOCs such as benzene, toluene, and xylenes are biodegradable, whereas, chlorinated VOCs are regarded as recalcitrant. However, there is increasing evidence that some chlorinated VOCs are also amenable to biological degradation. The three Philadelphia plants studied by Hentz have a combined maximum capacity of 23.4 m^3/sec (500 mgd) and total VOC emissions were 9.16 Mg/yr. In another study, Chang et al. in Mihelcic et al. (1993) estimated that 13 out of 589 Californian POTWs emit more than 9.1 Mg of 16 targeted VOCs annually. Total VOC from WWT emissions data for California were not retrieved, but combined POTWs in Los Angeles County were estimated to emit 429 Mg annually.

NITROUS OXIDE

Nitrification and denitrification processes are an integral part of comprehensive WWT. Both processes are thought to be capable of producing N_2O, however, denitrification may be considered the dominant mechanism in N_2O formation (Debruyn et al., 1994). For both nitrification and denitrification a carbon source is required for cell growth and nitrification also requires oxygen. Nitrification ($NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^-$) is the first step in nitrogen removal and takes place in aerobic reactors such as trickling filters or rotating biological contactors, either separate or in combination with carbonaceous matter removal. Nitrifying bacteria are sensitive organisms and are extremely susceptible to a wide variety of inhibitors.

During denitrification (Equation 9), N_2O is formed as an intermediate product and is usually consumed within cells, although some species excrete N_2O without further reduction (Hanaki et al., 1992). Denitrification is the second step in nitrogen removal and takes place under anoxic conditions. The presence of dissolved oxygen will inhibit the process, however, denitrification may not be described as an anaerobic process. The biochemical pathways are modifications of aerobic pathways (Metcalf and Eddy, 1991). As with nitrification, denitrification organisms are sensitive to changes in temperature and pH. Usually, an extra carbon source is required for cell growth.

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2 \qquad (9)$$

Hanaki et al. (1992) researched N_2O emissions during denitrification from wastewater under steady-state, laboratory conditions. Substrate containing acetate and yeast extract (1,000 ml COD), and potassium nitrate as a nitrogen source was continuously fed to three liter flasks containing return activated sludge from a WWT plant. The potassium nitrate concentration, pH, and hydraulic retention time (HRT) were varied in different experiments. It was found that favorable conditions for N_2O production

were a relatively low pH, a low COD/nitrogen (as NO_3) ratio, and a short HRT (i.e., less than one day). At pH = 6.5, N_2O production was significantly higher than at pH = 7.5.

Hanaki et al. conducted four sets of tests with COD/nitrogen (as NO_3) ratios[6] of 4.5, 3.5, 2.5, and 1.5, respectively and HRTs varying from 0.5 to 10 days. The pH of the substrate was between 7.5 and 8.5. With a COD/nitrogen (as NO_3) ratio of 4.5, no N_2O was detected in the emitted gas at any point during the experiment. With the COD/nitrogen (as NO_3) ratio being 3.5, approximately 1 percent of N_2O and 99 percent N_2 was detected in the early part of the test. With the COD/nitrogen (as NO_3) ratio being 1.5 and a HRT of 5 days, the percentage of N_2O peaked at 19 percent, but decreased again to 11 percent toward the end of the test.

Next, Hanaki et al. extended the HRTs for the tests with COD/nitrogen ratios of 1.5 and 2.5. For the COD/nitrogen = 1.5 test, increase of the HRT from 5 to 7 days resulted in a rapid decrease of the N_2O concentration from 11 percent to 6.5 percent. Further increase of the HRT to 10 days resulted in final N_2O concentrations of less than 0.6 percent (COD/nitrogen = 1.5 test) and 0 percent (COD/nitrogen = 2.5 test).

Knowledge acquired by Hanaki et al. indicates that N_2O production probably cannot easily be related to one single parameter of the wastewater, such as nitrogen concentration. N_2O is an intermediate product formed during denitrification and its formation and emissions are dependent on the incompleteness of various denitrification reactions that are governed by parameters that include pH, HRT, and feed concentrations.[7] Consequently, it will be difficult to develop accurate emission factors. The emission factor expressed by Hanaki et al. is 0.13 gram N_2O per gram nitrogen (as nitrate). Unfortunately they do not provide other wastewater data that allow for the development of more practical emission factors for estimating country-specific emissions (e.g., N_2O per COD or per capita).

In another study by Debruyn et al. (1994), wastewater samples were collected at three different WWT plants. Two of these plants treated mainly domestic wastewater, the third plant accepted a mix of industrial and agricultural wastewater. Twenty-one samples were kept under laboratory conditions at 25°C and the N_2O concentration in the head-space of the bottles was monitored. Since the initial rate of N_2O formation in the head space is representative of the rate of formation in an open undisturbed system, this initial rate may be used to develop an emission factor. In order to extrapolate the initial gas production rate to an overall emission factor, Debruyn et al. use a theoretical biochemical model referred to as the Michaelis-Menten formalism. This approach produces an emission calibration curve for a given wastewater composition and temperature (i.e., 25°C). By integrating the calibration curve with the Arrhenius equation

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[6] The COD/nitrogen (as NO_3) ratio in wastewater is a basic factor governing the completeness of nitrogen oxides reduction. If the reduction is not complete, N_2O will be formed. For actual denitrification, a ratio of at least 3.5 is necessary to permit cell matter build-up.

[7] Hanaki et al. concluded that N_2O production can be avoided by achieving complete denitrification by assuring high COD/NO_3-N concentrations, long HRTs, and neutral to alkaline pH.

(which expresses gas production as a function of chemical activation energy and temperature) it is theoretically possible to produce an N_2O emission factor.

Debruyn et al. proceed with statistical manipulation of the data and ultimately produce two rough indicative emission factors for Belgian sewage water which has a yearly mean temperature of 12.5°C. For raw wastewater, the emission factor is 23 ± 21 μg N_2O/g suspended solids (SS), and for wastewater, sampled after the settling tanks, the emission factor is 770 ± 170 μg N_2O/g SS. The combined total emission factor is 0.8 ± 0.2 mg N_2O/g SS.

In another study Czepiel and others monitored N_2O emissions at an activated sludge POTW in Durham, NH (Czepiel et al., 1995). As did Debruyn et al., and Hanaki et al., Czepiel et al. conclude that N_2O is generated in anaerobic sections of the WWT layout as an intermediate byproduct of denitrification. Potential sources are sewer lines, primary settling tanks, secondary clarification tanks, sludge holding tanks, and sludge transfer pipes. At the Durham POTW it was found that mechanical aeration (stripping) was a key release mechanism for N_2O. Czepiel et al. (1995) emphasize that they found no correlation between temperature and N_2O emissions. Emission factors derived from the Durham field tests include per capita emissions of 3.2 g N_2O/yr and flow based emissions of 1.6×10^{-5} g N_2O/l of wastewater treated for an activated sludge system. Expressed per gram of SS, the emission factor is 0.14 mg/g SS.

EMISSION FACTORS

Table 9 includes the available emission factors for GHGs from WWT. As mentioned in the previous chapter, conclusions of the field test report assert that anaerobic lagoons are a significant source of CH_4 emissions and that facultative lagoons that treat municipal wastewater are not a significant source of any GHGs, with the possible exception of CO_2.

METHANE AND CARBON DIOXIDE

CH_4 emission factors based on theoretical models and on empirical industrial digester data are within the range of 0.11 to 0.25 g/g COD. The lowest value is for industrial yeast production wastewater, and the highest value is for brewery wastewater. Toprak found an emission factor of 0.1 g/g COD for a municipal lagoon, which is lower than the other emission factors for domestic wastewater. Toprak's lower value may possibly be explained by an anticipated strong effect of local weather (rain, wind, ambient air temperature) on dissolved oxygen levels and, hence on CH_4 generation and emission rates. Also, the lagoon water temperature varied from 17.3 to 25.3°C; the 17.3°C value is considerably lower than the minimum for CH_4 generation conditions.

The average CH_4 emission factor (0.96 g/g COD) based on the APPCD field tests is higher than all other values, although the lower range of the field test factor (0.26 g/g COD) is within the range of the other data. The emission factor developed from the poultry processing lagoon data is higher than the ones from the two meat processing wastewater lagoons. If the data from the poultry processing lagoon are excluded, the average emission factor based on the field tests would be 0.42 g/g COD.

The most likely explanation for the fact that the average APPCD field test emission factors are higher than other factors from the literature is that the field test emission rates also account for CH_4 emissions from COD that had been deposited in the sludge during the previous winter. Appendix C contains a discussion on the effect of water and ambient air temperature on CH_4 emissions and COD removal rates in anaerobic lagoons. Based on this information, it is possible that emissions from a lagoon in summer in a mediterranean climate (hot summers and fairly cold winters), such as in the field test areas, are significantly higher than the yearly average.

For the purpose of developing CH_4 emissions estimates for this report, a CH_4 emission factor of 0.3 ± 0.1 g/g COD was used. This factor reflects the upper end of the range of factors based on theoretical models and empirical digester data, and the lower end of the range of the factors developed from the field test results.

The field test report is inconclusive about CO_2 emissions from anaerobic lagoons. Instead, a theoretical emission factor for CO_2 emissions from wastewater was used, which is included in Table 9.

TABLE 9. SUMMARY OF AVAILABLE EMISSION FACTORS

GAS	REFERENCE	D/I[1]	TYPE OF STUDY	REMARKS	EMISSION FACTOR[2]
CH_4	This report	D	Theoretical	Anaerobic	0.21 to 0.25 g/g COD
	Eklund and LaCosse, 1997	I	Field tests APPCD	Meat processing. Anaerobic lagoons	0.26 - 2.0 g/g COD
	Orlich, 1990; EPA,1994	D	Limited field study	Based on glucose. Lagoons	0.22 g/g BOD
	Toprak, 1995	D	Field tests	Anaerobic lagoon	0.10 g/g COD
	Paques, 1994	I	Empirical	Anaerobic digesters. Six types of industrial wastewater.	0.11 to 0.25 g/g COD
	Lexmond and Zeeman, 1994	I	Full- and pilot-scale digesters	Food & Beverage industry	0.22 g/g COD
				Pulp & Paper industry	0.019 g/g COD
	Czepiel et al., 1993	D	Field tests	Activated sludge plant.	1.7×10^{-3} g/g BOD_5
CO_2	This report	D	Theoretical	Aerobic	1.37 g/g COD
N_2O	Eklund and LaCosse, 1997	I	Field tests APPCD	Chicken processing, Anaerobic lagoon	1,700 mg/g TKN
					51 mg/g BOD
					89 mg/g COD
					76 mg/g TSS
	Schön et al., 1993	D/I	Comprehensive literature study	Plants that employ nitrification/ denitrification. Anoxic process	0.08 mg/l wastewater
					7,000 mg/capita/yr
	Debruyn et al., 1994	D	Laboratory	Anoxic process Raw wastewater	0.023 mg/g TSS
				Secondary wastewater	0.77 mg/g TSS
	Czepiel et al., 1995	D	Field tests	Anoxic process Raw wastewater	0.007 mg/ g TSS
				Secondary wastewater	0.13 mg/ g TSS
				Overall	3,200 mg/capita/yr
					0.016 mg/l wastewater

[1] Domestic/Industrial wastewater.
[2] per unit removed.

VOLATILE ORGANIC COMPOUNDS

The field tests found no speciated VOC emissions and only emission factors for total VOCs were found in the literature. Total VOC emissions from municipal WWT plants

have been estimated as a part of several studies. Melcer (1994) describes results of the Joint Emission Inventory Program, a working group of 22 of the 23 major POTWs in the South Coast Air Basin. According to this program, POTWs in the Basin emitted 149 Mg/yr of VOCs which was less than 0.03 percent of basin wide emissions. As a comparison, the two largest sources in California, solvent utilization and highway vehicles, were estimated to emit 517,093 and 662,241 Mg in 1991 (U.S. EPA, 1993a). The biggest point source in the United States, a chemicals plant in Kentucky, emitted 22,680 Mg/yr directly to the air (U.S. EPA, 1993b). Hence, it may be concluded that domestic WWT is an insignificant source of total VOC emissions compared to other VOC sources, such as highway vehicles and solvents.

Certain types of industrial wastewater (i.e., from petroleum refineries) may be a significant source of VOC emissions. The Joint Emission Inventory Program (Melcer, 1994) found that two out of 22 POTWs tested produced unusually high VOC levels. These were the only two facilities that accepted petroleum refinery wastewater. However, even with the petroleum wastewater included, the POTW emissions remained significantly smaller than emissions from other sources. No further information was available to quantify VOC emissions from petroleum refinery wastewater.

Theoretically, relatively small emissions of specific VOCs from other industrial processes may also be significant, due to their relatively high global warming potentials (see Table 9). For example, dichlorodifluoromethane and trichlorofluoromethane have global warming potentials of 8,300 and 3,900 times that of CO_2, respectively. The question is, will these and other strong GHG/VOC end up in wastewater. The two aforementioned VOCs are primarily used as blowing agents (e.g., styrofoam production) and in chillers. These processes imply utilization of VOCs in a gaseous or volatile state and it is unlikely that substantial amounts of these compounds would find their way into wastewater streams. However, this assumption is based on expert judgement. To estimate speciated emissions from industrial sources, an in-depth study of the various industrial processes that use specific VOCs is required, accompanied by extensive testing. Nevertheless, it may be asserted that total VOCs from WWT are insignificant compared to other sources.

NITROUS OXIDE

As mentioned in the previous chapter, N_2O is an intermediate byproduct of decomposition of nitrogen bearing organic compounds (proteins and urea) in wastewater. N_2O is generated, as well as absorbed during denitrification and many uncertainties are associated with the development of reliable N_2O emission factors. Currently, not enough is understood about N_2O generation and emission mechanisms to develop easy-to-use N_2O emission factors for WWT.

The emission factors based on data from field tests (Table 9) reflect a completely anaerobic environment whereas the other emission factors from the literature pertain to anoxic processes as part of conventional WWT. Therefore, the field test emission factor and the group of literature emission factors are presented separately.

The N_2O field test emission factors are expressed as emissions per BOD, COD, total suspended solids (TSS), and TKN. However, this report includes only comprehensive COD data and as such, only the COD-based emission factor (i.e., 0.09 g/g COD) can be used to estimate emissions. As insufficient information is available regarding the uncertainties associated with the relationship between COD and N_2O emissions, estimates derived from the use of this emission factor will be speculative. This emission factor pertains to wastewater types that contain nitrogen, including: domestic sewage; meat, poultry, and fish processing; and dairy products. Other types of industrial wastewater are not expected to contain much nitrogen.

Debruyn et al. (1994) and Czepiel et al. (1995) present emission factors expressed in terms of N_2O emissions per g TSS for both raw and semi-treated domestic wastewater. Because each emission factor pertains to wastewater with different concentrations, the emission factors cannot be added together without further modification, nor can they be easily extrapolated. This report does not contain comprehensive TSS data and consequently, the emission factors based on TSS were not used.

Debruyn et al. (1994) present no other emission factors with a different format. However, Czepiel et al. (1995) modified the TSS emission factor to a per capita and per year (capita/yr) basis. Also Schön et al. (1993) include an N_2O emission factor on a capita/yr basis. The average emission factor based on Schön et al. (1993) and Czepiel et al. (1995) is 5.1 g/capita/yr for domestic wastewater that is treated in activated sludge WWT plants.

Table 10 shows the emission factors that are used in this report to calculate GHG emissions from WWT.

TABLE 10. RECOMMENDED EMISSION FACTORS

GHG	*EMISSION FACTOR*	*APPLICATION, REMARKS*
CH_4	0.3 ± 0.1 g/g COD	Based on theoretical mass balance, empirical, and field test data.
CO_2	1.37 g/g COD	Based on simplified theoretical mass balance.
N_2O	0.09 g/g COD	Anaerobic WWT. Large uncertainties.
	5.1 g/capita/yr	Generic emission factor for all wastewater treated with activated sludge processes.

ACTIVITY DATA AND METHODOLOGY DEVELOPMENT

This chapter presents the methodologies and activity data used to prepare country-specific CH_4, CO_2, and N_2O emission estimates for industrial and domestic WWT. No methodology was developed for estimating VOC emissions which are classified as GHGs from WWT because, as discussed in the previous chapter, no emissions data were found that could be used to prepare the estimates. The methodologies and activity data are discussed together because the methodologies are limited by the type and amount of activity data available.

Some of the data used for developing country-specific CH_4 emissions estimates can also be used to develop estimates for CO_2 and N_2O emissions based on emission factors that were not derived from the field tests. These estimates are limited to the multiplication of the emission factor with the appropriate activity data and do not require particular methodology development. The global CO_2 and N_2O emissions estimates are included in the next chapter with the country-specific CH_4 estimates.

Equation 10 represents a generic methodology applicable to both domestic and industrial wastewater. The emission factor to estimate CH_4 emissions from WWT is defined as a function of the amount of organic material that is biodegraded expressed in COD (g/yr).

$$CH_4\ Emissions = EF * 10^{-12} * P * Q * COD * TA \quad (Tg/yr) \qquad (10)$$

where:
- EF = Emission factor (g CH_4/g $COD_{removed}$);
- P = Population, or industry-specific product output (Mg/yr);
- Q = Wastewater outflow (m^3/capita/yr) or wastewater produced per unit of product (m^3/Mg);
- COD = Organics loading removed (g/m^3); and
- TA = Fraction of COD in wastewater treated anaerobically.

INDUSTRIAL WASTEWATER

Basically there are three interdependent types of activity data that must be quantified to estimate emissions from industrial WWT: country-specific, industry-specific, and treatment-specific data (see Figure 1). Area A in Figure 1 represents country-specific industrial outputs. Area B represents WWT methods that are typical for a certain country or larger geographical area. For example, in South East Asia, land may be unavailable for lagoons due to high population densities and industries would have to make use of on-site digesters or crude disposal means, such as outfalls. Area C represents WWT methods that may be considered typical for a certain industry.

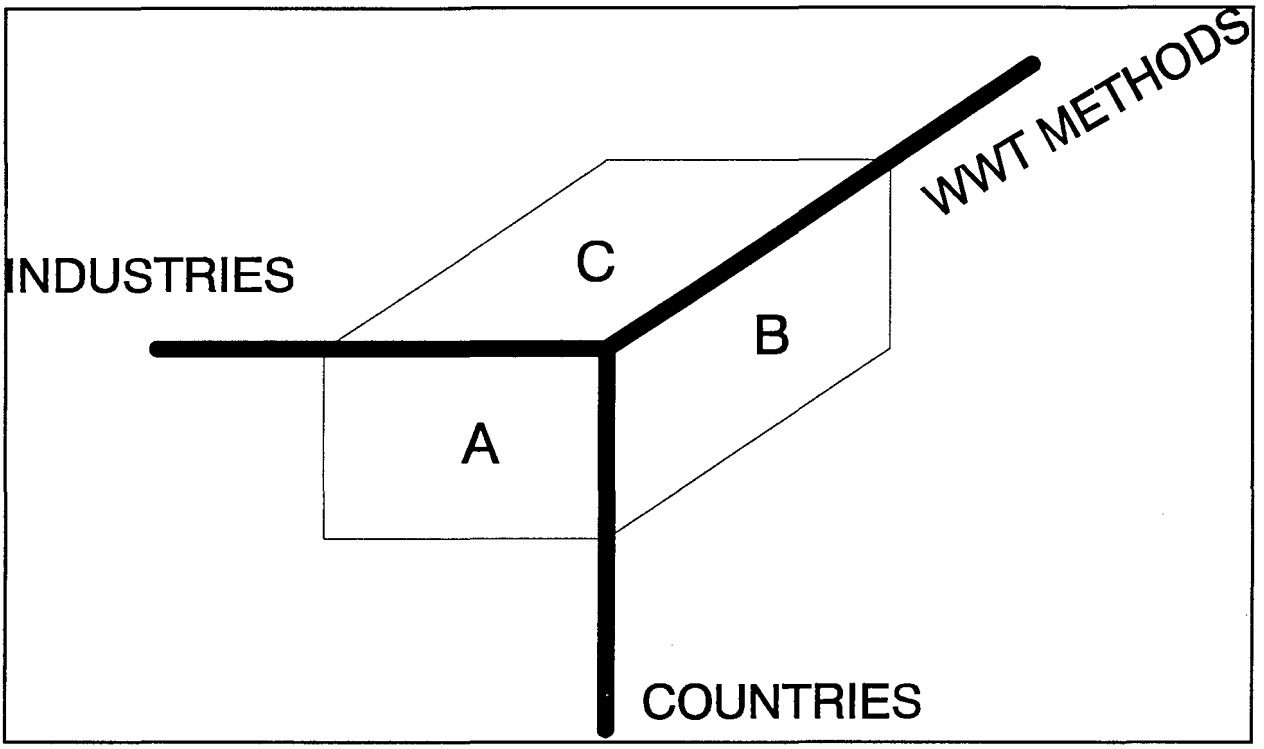

Figure 1. Parameters Used to Develop Emission Estimation Methodology for Industrial WWT.

For example, wastewater from the meat packing industry is known to decompose well under anaerobic conditions. It may be assumed that meat packing plants that do perform WWT are likely to make use of anaerobic techniques, regardless of their geographical location.

Below, a qualitative and quantitative determination is made of the industrial categories that generate wastewater with CH_4 emissions. Also, in this section a percentage to express the degree to which wastewater is treated anaerobically is assigned to each country-specific and industry-specific commodity output data combination.

Composition and Output

Industrial wastewater results from a myriad of industrial processes which use water for a variety of purposes, including production, refinement, transportation and handling. The water used in the various industrial processes is usually altered considerably and may contain contaminants including nutrients, SS, bacteria, and toxic substances, such as VOC and heavy metals. Large quantities of water are also used for cooling purposes, however, cooling water is not a potential source of GHGs. Some global and national estimates for total industrial wastewater generation were found in the literature (see Table 11).

TABLE 11. INDUSTRIAL WASTEWATER GENERATION ESTIMATES FOR THE UNITED STATES, CHINA, AND THE WORLD

COUNTRY	WASTEWATER GENERATION (10^6 m^3/day)	REFERENCE	REMARKS
United States	182	U.S. EPA; 1980	Manufacturing and minerals industry (1988 data).
United States	24	U.S. EPA; 1989	Industrial to municipal WWT plants. The difference with the above estimate implies a large degree of on-site industrial WWT.
China	71	Zhongxiang and Yi; 1991	74% discharged without treatment. Also report a domestic wastewater generation of 23 million m^3/day (1987 data).
World	1,300	U.S. EPA; 1994	Industrial wastewater outflow.
World	588	U.S. EPA; 1994	Same as above, but excluding Iron & Steel and Non-ferrous metals.

Wastewater generation can be expressed in liters per unit of product and varies from industry to industry. The amount, composition, and concentration of wastewater produced will depend on the type of product, the type of manufacturing processes, as well as process efficiency, regulatory requirements and compliance with the requirements, and good house keeping. Within the same industrial category in the same country, wastewater composition may also be highly variable. For example, wastewater from one pharmaceutical plant may be very different from wastewater from another pharmaceutical plant and will depend on the types of processes and raw materials used to manufacture various products. The production process may be batch-wise with different discharges of wastewater at different times and locations throughout the plant. There may also be more than one wastewater stream within a plant. For instance, at a food processing plant, highly contaminated process water may receive primary treatment on site, whereas water from rinsing operations with limited contamination may be discharged separately to the sewer.

Twenty-three industrial categories were identified as the potentially most significant dischargers of wastewater with high organic COD loadings (as opposed to inorganic COD loadings, such as metals). These 23 industrial categories are listed in Table 12. Typical wastewater generation rates expressed in m^3/Mg of product representative BOD and COD loadings are also included in Table 12. Industrial wastewater data provide indirect information on the efficiency of operation and on the plant output and are, therefore, often considered confidential by plants. Normally, only BOD_5, and to a lesser degree COD, are routinely measured by plant personnel. Fortunately, BOD_5 and preferably COD are also considered to be most practical for correlation with CH_4 generation.

TABLE 12. WASTEWATER OUTFLOW AND COMPOSITION DATA FOR SELECTED INDUSTRIES

INDUSTRY TYPE	WW Gen.	WW Gen. Range	WW Generation Reference	BOD	BOD Range	BOD Reference	COD	COD Range	COD Reference
units:	m^3/Mg	m^3/Mg		g/l	g/l		g/l	g/l	
Animal Feed	ndf			ndf			ndf		
Alcohol Refining	24	16-32	Curi, 1985; Metcalf & Eddy, 1991	ndf	3-11	extrapolated from COD data	11	5-22	Hulshoff Pol et al., 1986
Beer & Malt	6.3	5.0-9.0	Merritt, 1983; Jansen, 1994	1.5	1-4	Paques, 1994; Jansen, 1994; Merritt, 1983	2.9	2-7	Paques, 1994; Jansen, 1994; Hulshoff Pol, 1986
Coffee	ndf			5.4	2-9	Gathuo et al., 1991	9	3-15	Gathuo et al., 1991
Coke	1.5	1.3-1.7	Dulaney, 1982; Wurm, 1974	ndf	0.1	extrapolated from COD data	0.1		Wen et al., 1991
Dairy Products	7	3-10	Merritt, 1983; Metcalf & Eddy, 1991	2.4	1-4	Viraraghavan and Kikkeri, 1990	2.7	1.5-5.2	Viraraghavan and Kikkeri, 1990; Lettinga et al., 1980
Drugs & Medicines	ndf			0.9		Elsevier, 1991	5.1	1-10	Elsevier, 1991; Lanting and Franklin, 1993
Explosives	ndf			ndf			ndf		
Fish Processing	ndf	8-18	same as Meat & Poultry	1.5		Forsht, 1974	2.5		Forsht, 1974
Meat & Poultry	13	8-18	Eklund & LaCosse, 1997	2.5	2-3	Eklund & LaCosse, 1997	4.1	2-7	Eklund & LaCosse, 1997
Organic Chemicals	67	0-400	Hund & Forsht, 1987; Metcalf & Eddy, 1991	1.1	1-2	Hund & Forsht, 1987	3	0.8-5	Hund & Forsht, 1987; Wood, 1990
Paints	ndf	1-10	expert judgement	ndf			ndf	1-10	same as Drugs & Med.
Petroleum Refineries	0.6	0.3-1.2	Dennis, 1982	0.4	1-8	Dennis, 1982; Elsevier, 1991	1.0	0.4-1.6	Dennis, 1982; Elsevier, 1991
Plastics & Resins	0.6	0.3-1.2	same as Petroleum Refineries	1.4	1-2	Hund & Forsht, 1987	3.7	0.8-5	Hund & Forsht, 1987
Pulp & Paper (combined)	162	85-240	Weyerhaeuser, 1995; Merritt, 1983	0.4	0.3-8	Weyerhaeuser, 1995; Paques, 1994	9	1-15	Paques, 1994
Soap & Detergents	ndf	1.0-5.0	same as Vegetable oils	ndf	0.3-0.8	same as Vegetable oils	ndf	0.5-1.2	same as Vegetable oils
Soft Drinks	ndf	2.0	expert judgement	ndf	1.0	expert judgement	ndf	2.0	expert judgement
Starch Production	9	4-18	Curi, 1985	2.0	1-25	Paques, 1994	10	1.5-42	Paques, 1984; Hulshoff Pol et al., 1986
Sugar Refining	ndf	4-18	same as Starch Prod.	ndf	2-8	extrapolated from COD data	3.2	1-6	Lettinga et al., 1980
Textiles (natural)	172	100-185	Brown, 1995; Gorsuch, 1982	0.4	0.3-0.8	Brown, 1995; Gorsuch, 1982	0.9	0.8-1.6	Brown, 1995; Dulaney, 1982
Vegetable Oils	3.1	1.0-5.0	Merritt, 1983	0.5	0.3-0.8	Merritt, 1983, Amstel et al., 1987	ndf	0.5-1.2	extrapolated from BOD data
Vegetables, Fruits & Juices	20	7-35	Merritt, 1983; Metcalf & Eddy, 1991	1.0	0.5-2	Merritt, 1983	5.0	2-10	Lettinga et al., 1980
Wine & Vinegar	23	11-46	expert judgement	0.7	0.2-1.4	expert judgement	1.5	0.7-3.0	expert judgement

Notes: ndf = no data found

When no multiple data are available, the range is assumed to be -50/+100%

Wastewater outflows can be obtained by multiplying industry-specific production outputs with generation rates (m^3/kg product). Country-specific annual industrial output data are compiled by the United Nations and published in the Industrial Statistical Yearbook (United Nations, 1992a and United Nations, 1992b). Country-specific commodity production outputs per industry category for 1990 are included in a large spreadsheet, named UNISY (after the yearbook) which is not included in this report.

Earlier CH_4 emission estimates by EPA (U.S. EPA, 1994) included iron and steel wastewater as a separate category but, according to Olin et al., (1987), 99 percent of the organic loading in wastewater from iron and steel mills results from coke manufacturing. Accordingly, coke manufacturing was added in Table 12 , instead of iron and steel. However, the United Nations Statistical Yearbook only provides data for iron and steel and not for coke making. The world coke output was calculated by using a coke-to-iron ratio based on data from Quarterly Coal Report (DOE 1993) in combination with U.S. and world iron and steel output data. Strictly speaking, coke consumption should only be related to pig iron manufacturing and not to steel manufacturing. As no separate iron and steel data were available, this distinction is ignored.

The UNISY did not provide data for the petroleum refining category and instead information from Petroleum Supply Annual (U.S. DOE, 1990) was used. According to Petroleum Supply Annual, the finished petroleum products output for 1990 was 715 Tg. To produce an estimate for the output for the rest of the world, it was assumed that the United States produces 33 percent of all petroleum products.

Data reduction on UNISY was performed by eliminating all countries with populations less than one million.[8] Also, the animal feed, coffee processing, drugs and medicines, and explosives categories were eliminated, because they have relatively minor industrial outputs according to UNISY. For example, both the coffee industry and the vegetable oil industry are known for their highly concentrated wastewater, but the total world coffee production is only 1 percent of vegetable oil production and thus relatively minor. As the UNISY data base contains over 100 countries, and each country may represent several or most industrial categories, further data reduction was necessary. Between two and four Major Producing Countries for each industrial category were identified and all other countries were labeled "rest of the world." The major producing countries represent between 50 and 75 percent of world total for that particular industry.

In order to assign a numerical value to the prevailing industry-specific and country-specific WWT methods, the targeted industries from Table 12 first were classified into five groups: Animal Products; Industrial Plant Processing; Vegetables, Fruits and Textiles; Pulp and Paper; and Organic Chemicals and Related Products. Industries within each group are considered to generate wastewater that is comparable in chemical, biological, and physical composition, as well as by overall treatment method or lack thereof.

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[8] A total of 61 countries was eliminated, representing a population of 14 million. Most countries that were eliminated are so-called island states.

For each of these five groups the country- or region-specific percentage of on-site treatment was estimated, compared to raw discharge or discharge into sewers. Next, the fraction of organic matter treated anaerobically was estimated. Both estimates were combined into a single factor TA_{ic} which expresses the country or region-specific fraction of wastewater for each industrial group that is treated at the industrial site under anaerobic conditions. Estimates for TA_{ic} for each of the five industry categories are included in Table 13, as well as the general assumptions used. TA_{ic} includes three types of on-site anaerobic treatment conditions: intended anaerobic treatment in a wastewater digester or lagoon; sludge storage and handling;[9] and undesired anaerobic conditions, as a result of overloading or mismanagement.

The five aforementioned industrial groups are described below in detail. The methodology for calculating CH_4 emissions from industrial wastewater used in this report, as adapted from Equation 10, is presented in the next chapter in combination with the emission estimates.

Group 1. Animal Products–

This group includes the meat, poultry, dairy, and fish processing industries. Wastewater from these industries is high in animal proteins and fats. It usually is relatively strong with high BOD and total organics loadings. In many countries, most cattle and poultry slaughtering and also dairy production is expected to be small scale, taking place at the farm or the home. Wastewater associated with home slaughtering or creaming would be classified as domestic wastewater. It is assumed that the UNISY commodity numbers do not reflect these small scale activities and purely relate to industrial operations.

In developed countries and perhaps also in some developing countries industrial meat packing plants (including tanneries) and poultry processing plants are often large-scale operations, generating proportionally large wastewater outflows. These plants, typically provide primary WWT that would include anaerobic lagoons. Secondary treatment would consist of facultative lagoons, after which the treated wastewater is land applied or otherwise discharged.

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[9] Actual anaerobic sludge treatment is not included as a CH_4 source, although the emission factors used in this report to account for some sludge storage and handling. Up to 40 percent of COD (in an aerobic WWT process) may be turned into sludge. Sludge is removed from the site to be dumped elsewhere (landfills or oceans) or it may be treated on site by various methods. According to Metcalf & Eddy (1991, p. 814), anaerobic sludge digestion is the dominant sludge stabilization process. The digestion process generates significant amounts of CH_4 and is designed to recover and utilized or flare the CH_4. Some CH_4 from anaerobic sludge digesters may however, leak to the atmosphere. Detailed research on CH_4 or other GHG emissions from sludge treatment is beyond the scope of this report.

TABLE 13. GLOBAL WASTEWATER DISCHARGE AND TREATMENT PRACTICES

MEAT, POULTRY, DAIRY, AND FISH PROCESSING INDUSTRY						
Country	*Raw Discharge**	*To sewers or treated on site*	*Treated on Site*	*Treated on Site (anaerobic)*	*TA_{ic}***	*Discharge to city sewers*
	(%)	(%)	(%)	(%)	(%)	(%)
	A	100-A	B	C	(100-A)*B*C	(100-A)(100-B)
Africa	60	40	95	90	34	2
Japan (other than fish)	10	90	80	90	65	18
Japan (fish)					10	
Other Asia	70	30	80	90	22	6
Russian Federation	50	50	50	90	23	25
Germany	0	100	80	90	72	20
United Kingdom	0	100	80	90	72	20
France	0	100	80	90	72	20
Italy	0	100	80	90	72	20
Other OECD	0	100	70	90	63	30
Other Europe	50	50	50	90	23	25
United States	0	100	85	90	77	15
Canada	0	100	85	90	77	15
Latin America	50	50	70	90	32	15
Australia	0	100	80	90	72	20
Average Rest of the World						3512

Notes

Percentages reflect amounts of COD and not volumes of water.

* To surface water or land "treatment."

** TA_{ic} = the country or region-specific fraction of wastewater for each industrial category that is treated at the industrial site under anaerobic conditions.

References: Draaijer, 1994; Doppenberg, 1994; Wiegant and Kalker, 1994; and Lexmond and Zeeman, 1995.

General Assumptions

Anaerobic lagoons are common for this category.

Throughout the world, a considerable amount of activity for these industrial categories may take place at a very small scale (e.g., home slaughtering).
It is assumed that the commodity output numbers do not reflect small scale processing.
Nor do the assumptions for WWT practices.

It is assumed that most Japanese fish waste is dumped in the sea.

It is assumed that all large operations in developed countries have their own primary treatment facilities.
Hence the relatively low "Raw Discharge" values and the relatively high "Treated on Site" values.
High column B numbers for some countries are indicative of the absence of sewers.

TABLE 13 (continued)

ALCOHOL REFINING, BEER, WINE, VEGETABLE OIL, SUGAR, AND STARCH INDUSTRIES						
Country	*Raw Discharge**	*To sewers or treated on site*	*Treated on Site*	*Treated on Site (anaerobic)*	*TA_{ic}***	*Discharge into city sewers*
	(%)	(%)	(%)	(%)	(%)	(%)
	A	100-A	B	C	(100-A)*B*C	(100-A)(100-B)
Africa	60	60	95	30	17	3
Japan	5	95	80	10	8	19
Other Asia	60	40	95	30	11	2
Russian Federation	20	50	50	30	8	25
Germany	0	100	40	10	4	60
United Kingdom	0	100	40	10	4	60
France	0	100	40	10	4	60
Italy	10	100	40	10	4	60
Other OECD	10	90	40	10	4	54
Other Europe	20	50	50	30	8	25
United States	0	100	80	10	8	20
Canada	0	100	80	10	8	20
Latin America	60	60	60	35	13	24
Australia	0	100	80	10	8	20
Average Rest of the World						1110

Notes

Percentages reflect amounts of COD and not volumes of water.

* To surface water or land "treatment."

** TA_{ic} = the country or region-specific fraction of wastewater for each industrial category that is treated at the industrial site under anaerobic conditions.

References: Draaijer, 1994; Doppenberg, 1994; Wiegant and Kalker, 1994; and Lexmond and Zeeman, 1995.

General Assumptions

Aerobic (aerated) lagoons most are common for this category.

In developed countries, in some cases anaerobic digesters are also used.

Raw or semi-raw wastewater is often discharged into sewers for treatment at the local POTWs.

Except for wineries and some breweries, these industries are typically large, often multi-national operations that are assumed to have their own primary or comprehensive WWT.

Relatively high values in column C for developing countries indicate assumed anaerobic conditions resulting from possible overloading and/or underaeration.

TABLE 13 (continued)

VEGETABLES, SOFT DRINKS, JUICE, AND TEXTILE INDUSTRIES						
Country	*Raw Discharge**	*To sewers or treated on site*	*Treated on Site*	*Treated on Site (anaerobic)*	*TA_{ic}***	*Discharge into city sewers*
	(%)	(%)	(%)	(%)	(%)	(%)
	A	100-A	B	C	(100-A)*B*C	(100-A)(100-B)
Africa	70	30	95	20	6	2
Japan	10	90	10	10	1	81
Other Asia	70	30	80	20	5	6
Russian Federation	50	50	5	20	1	48
Germany	0	100	5	0	0	95
United Kingdom	0	100	5	0	0	95
France	0	100	5	0	0	95
Italy	10	90	5	0	0	86
Other OECD	10	90	5	15	1	86
Other Europe	50	50	5	20	1	48
United States	0	100	5	0	0	95
Canada	0	100	5	0	0	95
Latin America	60	40	60	20	5	16
Australia	0	100	5	0	0	95
Average Rest of the World						430

Notes

Percentages reflect amounts of COD and not volumes of water.

* To surface water or land "treatment."

** TA_{ic} = the country or region-specific fraction of wastewater for each industrial category that is treated at the industrial site under anaerobic conditions.

References: Draaijer, 1994; Doppenberg, 1994; Wiegant and Kalker, 1994; and Lexmond and Zeeman, 1995.

General Assumptions

Typically wastewater from these categories is directly discharged to sewers to be treated at POTWs. (Low "Treated on Site" values for developed countries.)

For developing countries column B values are high, implying that if there is treatment it will be at the industrial site, since there are no city sewers.

In developing countries, where there are no sewers/POTWs, lagoons may be common.

Relatively high "Treated on Site (anaerobic)" values for developing countries, account for possible anaerobic situations due to overloading or underaerating.

TABLE 13 (continued)

PULP AND PAPER INDUSTRY						
Country	*Raw Discharge**	*To sewers or treated on site*	*Treated on Site*	*Treated on Site (anaerobic)*	*TA_{ic}***	*Discharge into city sewers*
	(%)	(%)	(%)	(%)	(%)	(%)
	A	100-A	B	C	(100-A)*B*C	(100-A)(100-B)
Africa	25	75	100	20	15	0
Japan	0	100	100	1	1	0
Other Asia	25	75	100	20	15	0
Russian Federation	20	80	100	25	20	0
Germany	0	100	100	1	1	0
United Kingdom	0	100	100	1	1	0
France	0	100	100	1	1	0
Italy	0	100	100	1	1	0
OECD	5	95	100	1	1	0
Other Europe	10	90	100	15	14	0
United States	0	100	100	1	1	0
Canada	0	100	100	1	1	0
Latin America	25	75	100	20	15	0
Australia	0	100	100	1	1	0
Average Rest of the World						120

Notes

Percentages reflect amounts of COD and not volumes of water.

* To surface water or land "treatment."

** TA_{ic} = the country or region-specific fraction of wastewater for each industrial category that is treated at the industrial site under anaerobic conditions.

References: Draaijer, 1994; Doppenberg, 1994; Wiegant and Kalker, 1994; and Lexmond and Zeeman, 1995.

General Assumptions

Aerobic (aerated) lagoons are common for this category.

Large multi-national companies assumed to have adequate WWT.

Also, it is assumed that pulp and paper plants are not typically located near cities and, therefore, conduct their own WWT.

Relatively high values in column C for developing countries indicate assumed anaerobic conditions resulting from possible overloading and/or underaeration.

TABLE 13 (continued)

ORGANIC CHEMICALS, PETROLEUM REFINING, PLASTICS AND RESINS, COKING, DETERGENTS, PHARMACEUTICALS, AND PAINT INDUSTRIES						
Country	*Raw Discharge**	*To sewers or treated on site*	*Treated on Site*	*Treated on Site (anaerobic)*	*TA_{ic}***	*Discharge into city sewers*
	(%)	(%)	(%)	(%)	(%)	(%)
	A	100-A	B	C	(100-A)*B*C	(100-A)(100-B)
Africa	60	40	90	10	4	4
Japan	10	90	70	4	3	27
Other Asia	60	40	90	10	4	4
Russian Federation	50	50	50	10	3	25
Germany	0	100	70	4	3	30
United Kingdom	0	100	70	4	3	30
France	0	100	70	4	3	30
Italy	5	95	70	4	3	29
Other OECD	10	90	70	10	6	27
Other Europe	20	80	50	10	4	40
United States	0	100	80	4	3	20
Canada	0	100	80	4	3	20
Latin America	60	40	80	10	3	8
Australia	0	100	70	4	3	30
Average Rest of the World						310

Notes

Percentages reflect amounts of COD and not volumes of water.

* To surface water or land "treatment."

** TA_{ic} = the country or region-specific fraction of wastewater for each industrial category that is treated at the industrial site under anaerobic conditions.

References: Draaijer, 1994; Doppenberg, 1994; Wiegant and Kalker, 1994; and Lexmond and Zeeman, 1995.

General Assumptions

Typically chemical or physical primary treatment, followed with an aerobic phase.

In developed countries, effluent from primary treatment is discharged into sewers.

Typically large processing plants, in part multi-nationally owned, which are assumed to have adequate WWT.

In some countries dairy wastewater may be treated aerobically, and fish wastewater may be treated with physical purification methods, such as centrifuging. Fish and dairy operations are nevertheless classified with meat and poultry processing because of the similarities in biological and chemical composition. Errors resulting from the broadness of this classification are not expected to significantly affect emissions estimates, because commodity outputs for dairy products and processed fish are relatively small compared to poultry and meat outputs.

Group 2. Industrial Plant Processing–

This group includes alcohol, beer, wine, vegetable oil, sugar, and starch production. Processes associated with these industries involve the conversion of mono-culture crops to refined products. All processes, with the exception of vegetable oil production, are characterized by a refining or fermentation step in which the original raw material is modified extensively. Raw materials for the alcohol, beer, vegetable oil and starch production consist of grains or seeds. Sugar is made from cane or beets, the latter containing starch as raw material. Wine is the exception here, as its raw material is fruit, however, the extensive alteration and fermentation justifies its classification with alcohol and beer production.

Wastewater from this group is considered to be high in vegetable organics (as opposed to animal organics). Processing plants within this group (with the exception of some wineries and some European breweries) are usually large in size and produce proportionally large amounts of wastewater. In developing countries the plants are often foreign owned. Industrial categories that are foreign owned and that operate relatively large plants are assumed to have appropriate WWT. Comprehensive treatment or primary treatment (removing most organics) is, therefore, assumed to take place on site and usually is in aerated lagoons. However, certain steps in the treatment process may be anaerobic, for instance, due to under-aeration or overloading of lagoons. Values in the column entitled "Treated on Site (anaerobic)" in Table 13 reflect this possible condition for developing countries and Eastern European countries.

Group 3. Vegetables, Fruits and Textiles–

This group includes vegetable processing, juice and soft drinks production, and textiles. Wastewater from these industries is usually moderately contaminated with plant organics and is typically discharged into the public sewer system (if there is a sewer system) sometimes after preliminary treatment, such as screening. Textiles wastewater consists of dyes which may be chemically different from vegetable waste, although dyes made from plants are also popular. However, textile wastewater is also always discharged to public sewers and is also moderately polluted with organics (Brown, 1995).

Typically, industries in this group may vary significantly in size from large plants owned by multi-national corporations to small green-grocer type operations. Typical for this industry is that the wastewater outflows may be batch wise and that the wastewater composition and loading may vary significantly from batch to batch. A cannery or bottling hall would typically process a certain product, for one or several shifts, after which the lines are cleaned and a new type of product is started up. This is the reason that, even for modern operations, it is preferred to have the municipal WWT plant treat the wastewater, for then the concentration and outflow variations can be absorbed more

easily. Of course, as operations vary in size and the wastewater is not terribly strong, raw wastewater may also be discharged to surface water in certain countries.

Group 4. Pulp and Paper Industry–

Pulp and paper mills require large amounts of water and will always be situated on rivers. The industry produces large quantities of wastewater that is unique in composition (cellulose instead of starches and/or sugars). Due to their size, pulp and paper mills are often owned by large corporations. Large corporations, especially multi-national ones, are expected to receive more scrutiny from local governments, compared to small businesses. As a result, environmental clean-up efforts, including WWT, by large companies are expected to be fairly high throughout the world. Comprehensive treatment or primary treatment (removing most organics) is, therefore, assumed to take place on site and usually is in aerated lagoons. However, certain steps in the treatment process may be anaerobic, for instance, due to under-aeration or overloading of lagoons. Values in the column entitled "Treated on Site (anaerobic)" in Table 13 reflect this possible condition for developing countries and Eastern European countries. The percentage "Treated on Site (anaerobic)" for developed countries is assumed to be 1 percent and reflects anaerobic conditions that may occur in tertiary lagoons.

Group 5. Organic Chemicals and Related Products–

This group includes the organic chemicals, plastics and resins, petroleum refining, coking, detergents, pharmaceuticals, and paint industries. Facilities in this group are usually large in size and are owned by multi-national corporations. Wastewater is usually weak, but may also be moderately to very strong for the production of certain organic chemicals. It may likely contain VOCs, petroleum derivatives, and other substances that may be toxic to bacteria.

Typically, production plants use equalization basins or stabilization ponds to reduce variations in composition and concentration of the wastewater and to allow for any possible (aerobic) biological break down of susceptible organics. However, compared to the other groups wastewater from this group is likely to vary significantly in composition. As a result, WWT methods are also highly diverse, including different types of physical and chemical treatment, as well as, aerobic treatment (e.g., in trickling filters). Anaerobic treatment is generally not well suited for this group, because anaerobic bacteria are vulnerable to composition variations and are easily upset by inhibitory compounds in the wastewater, which include, but are not limited to certain salts containing heavy metals and/or sulfides, and anthropogenic VOCs. (Alabaster, et al., 1991.) In developed countries, preliminary treatment may be at the industrial site, after which the wastewater is invariably discharged into the public sewer. In developing countries all treatment may be at the site or other scenarios may exist that range between raw discharge to full treatment. It was assumed that between 4 and 10 percent of treatment at the site is anaerobic, reflecting the possible use of digesters as well as possible overloading of lagoons.

Industrial Wastewater Discharged to City Sewers

Often, raw industrial wastewater or industrial wastewater that underwent preliminary treatment at the industrial site is discharged into city sewers. In the sewer

line systems and ultimately at the WWT plant (if present) this industrial wastewater will become thoroughly mixed with domestic wastewater. Industrial wastewater that is discharged into city sewers is classified as domestic wastewater in this report.

In countries with wastewater regulation enforcement, industrial wastewater discharges into sewers are limited to biologically treatable waste, in order not to affect the WWT system at the municipal WWT plants. In other countries where there may be little or no enforcement, any type of wastewater may be discharged into sewers, which may result in impeding proper functioning of the municipal WWT plants. Table 13, which defines global wastewater discharge and treatment practices for the five aforementioned industry groups also includes country-specific estimates of the fraction of industrial wastewater (expressed in COD) that is discharged into city sewers.

DOMESTIC WASTEWATER

Composition and Output

Domestic wastewater is the spent water originating from all aspects of human sanitary water usage. Domestic wastewater contains components that are typically organic in nature (carbohydrates, lipids, proteins, soaps) and it may be considered somewhat homogeneous. An average composition is given in Table 14. It is typically generated from households from the use of toilets, baths, laundry, and kitchens. Domestic wastewater sources include sources other than households, such as institutions, offices, shops, schools, and recreational facilities. Municipal WWT plants that treat domestic wastewater typically employ biological, aerobic treatment. (Appendix B includes generic information on municipal sewage treatment operations.)

In order to develop emissions estimates from domestic WWT three methods were evaluated for estimating organic domestic wastewater loadings were evaluated: (1) the use of water consumption data; (2) the use of wastewater generation data; (3) the use of per capita organics loadings.

Generic water consumption data are available from various handbooks, for example, the World Resources Institute publishes country-specific per capita water consumption rates (World Resources Institute, 1994). Adjustments may be made by estimating the water consumption at the house (e.g., lawn watering) and water losses and/or gains in sewer lines (leakages, influx of storm- or groundwater).

TABLE 14. TYPICAL COMPOSITION OF UNTREATED DOMESTIC U.S. WASTEWATER

POLLUTANT	RANGE (mg/L)	POLLUTANT	RANGE (mg/L)
Solids Total	730-1,180	Total Organic Carbon	200-500
Dissolved, Total	400-700	COD	550-700
Mineral	250-450	Total Nitrogen (as N)	40-50
Organic (Volatile)	150-250	Organic	15-20
Suspended	180-300	Free ammonia (NH_3)	25-30
Mineral	40-70	Nitrates and Nitrites	0
Organic	140-230	Total Phosphorus (as P)	10-15
Total Settleable Solids	150-180	Chlorides	50-60
BOD_5	160-280	Alkalinity [as calcium carbonate ($CaCO_3$)]	100-125
Trace amounts of paints, motor oils, nail polish removers, etc.	< 1	Oil and Grease Typical pH	90-110 7.0-7.5

Based on Mullick (1987). Assumptions are: water consumption of 100 gallons (380 l) per capita, no industrial wastewater, median use of garbage disposals, and moderate income population.

Non-industrial per capita water use rates for the United States lie between 100 and 166 gallons [380 and 630 liters (l) per day] (Mullick, 1987; Corbitt, 1990; and Metcalf & Eddy, Inc., 1991). It is estimated that 60 to 85 percent of water used becomes wastewater, largely depending on lawn watering requirements (Metcalf & Eddy, 1991). This converts into a daily per capita domestic wastewater generation rate of around 60 to 141 gallons (228 to 536 l). The amount of wastewater produced can be multiplied with the average organics concentration to obtain organics loadings. This method is not considered very reliable, because it is difficult to estimate which fraction of the water consumed will become wastewater. In addition, wastewater quantities may increase considerably as a result of the inflow of stormwater into the sewer systems.

Next it was attempted to base the methodology directly on wastewater generation rates. However, except for the United States,[10] sparse information is available on domestic wastewater generation rates. Some studies provide data that pertain to specific sites. For example, Toprak (1993) gives a number of 200 l per day per capita for the city of Izmir, Turkey, but such a local rate may not be representative for the whole country. Also, some handbooks provide generic wastewater generation rates, as well as average composition data. Country-specific per capita wastewater generation rates are likely to vary significantly, depending on local climate, cultural habits, and economic levels. As

[10] According to the 1988 Needs Survey (U.S. EPA, 1989), there were 15,711 POTWs in operation in the United States in 1988, serving a population of 176 million, and treating 37,866 million gallons per day (MGD) of wastewater and possibly some stormwater. The rest of the population would have septic systems, or no treatment. About 17 percent or 6,437 MGD of this wastewater was considered to be industrial with the other 31,429 MGD being commercial and domestic wastewater.

with wastewater quantities generated from water consumption rates, it is difficult to estimate the influence of stormwater inflow.

Given the uncertainties associated with the use of water consumption and wastewater generation rates, it was preferred to look directly at organics loadings expressed in grams of BOD_5 per capita/day. The quantity of organic waste products in the wastewater is independent of stormwater inflow or other types of dilution. Table 15 contains BOD_5 loadings for different regions in the world, which are largely dependent on diet, metabolism, and body weight. An advantage of this method is that a per capita discharge rate is not likely to be independent of the person's location (e.g., home or office). OECD countries were grouped together, although the United States is in a category by itself. The higher U.S. number is due to widespread use of garbage disposals in the United States.

TABLE 15. BOD_5 AND COD LOADINGS FOR DIFFERENT REGIONS OF THE WORLD

	BOD_5 LOADING[1] (g/capita/day)	*COD LOADING[2] (g/capita/day)*
Developing Countries	35 ± 10	90 ± 40
Eastern European Countries	45 ± 10	110 ± 45
OECD Countries (except U.S.)	55 ± 15	140 ± 65
United States	65 ± 15	160 ± 70

[1] Based on Lexmond and Zeeman (1995); Metcalf & Eddy (1991); Mullick (1987); U.S. EPA (1994), and Polytechnisch Zakboekje (1984).

[2] COD/BOD ratio = 2.5. See Table 1. Values are rounded to nearest 10.

Extent of Sewerage, Treatment, and Prevailing Treatment Methods

In many developing countries, sewerage infrastructure does not reach large sections of the population. Especially in rural areas and urban slums, sewerage is virtually nonexistent (WHO/UNICEF, 1993; Draaijer, 1994). In rural areas, the lack of sewerage is not necessarily a problem and people use designated areas of the surrounding land (Marks, 1993). Also, domestic sewage may be treated on the premises in pit latrines or septic sewage systems. As previously discussed, emissions from untreated wastewater and wastewater treated in latrines and septic tanks are not addressed in this report. As population densities increase, lack of adequate sanitation, including sewerage may become a health issue and the concentration of untreated sewage may be a source of GHGs.

Often, official published figures are flattered. For example, slum dwellers may not be included, or people with bucket latrines may be counted as served by WWT (Bartone, 1990). For the mid-eighties, it was estimated that in Africa only 14 percent of the urban population has a sewerage connection. In Latin America and the Middle East, official figures indicate that 41 percent of the urban population has sewers (capitals or other

large cities 50 to 85 percent; for secondary cities this number is less than 10 percent). For Asia and the Pacific, less than 20 percent of the total urban population has sewer-to-house connections (Bartone, 1990). Figure 2 provides an overview of sanitation by technology type based on a survey of 63 developing countries (WHO/UNICEF, 1993).

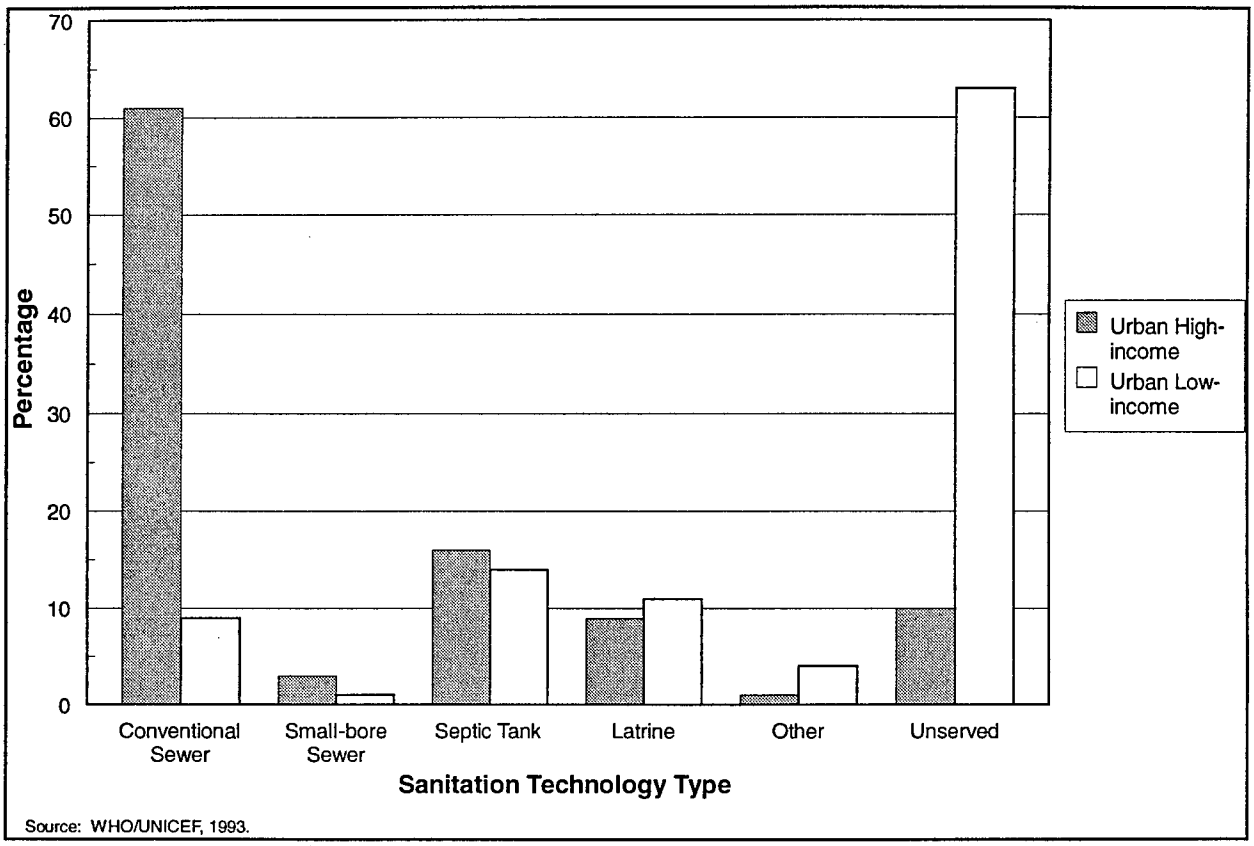

Figure 2. Urban Sanitation by Technology Type

When there are sewer lines but no treatment facilities, the raw sewage is discharged into a river, lake, or ocean. Pipes that transport raw sewage some distance from the coast and discharge it below sea level are called outfalls. Outfalls are used all over the world for wastewater discharge, with the exception of wealthy OECD countries (Draaijer, 1994). Andreadakis et al. (1993) report that the city of Thessaloniki in Greece (100,000 inhabitants) uses an outfall to discharge raw sewage. There is a primary treatment plant that is inoperative because effluent standards are not being met. An outfall that serves part of Rio de Janeiro, Brazil dumps an average of 6 m^3/sec (136 MGD) of raw wastewater into the Atlantic Ocean (Jordao and Leitao, 1990). Organics that are discharged into rivers, lakes, or oceans are not considered to contribute to the GHG effect, because they are assumed to be facultative.

On its way to the discharge location sewage may undergo significant biodegradation depending on residence time and temperature. The residence time may be high or even infinite due to poor design and overloading of the sewer system. In developing countries, sewers may be mere open gutters which are prone to clogging as a result of dumping of solid waste (Doppenberg, 1994; Wiegant and Kalker, 1994). Stagnant sewage, especially in warm countries will rapidly turn septic and is thought to be a significant source of CH_4 (Draaijer, 1994).

Whereas, country-specific data on the extent of sanitation, including sewer connections are fairly easily obtained, very few literature sources exist that give numerical information on the extent of WWT. Country-specific data on the extent of WWT were found for China. The Chinese Government estimates that 31.7 gigagrams (Gg) of wastewater (including 23.9 Gg of industrial wastewater) is produced annually. About 74 percent of this is discharged without treatment. In 1984, sewage disposal in urban Beijing was about 700 million m^3/yr, of which only 15 percent was treated. A WWT plant of 500,000 m^3/day is planned to come on line in 1990, which would cover 42 percent of the wastewater outflow. (Zhongxiang and Yi; 1991.)

In developed countries, the extent of wastewater treatment is generally higher than in developing countries. Table 16 gives an overview of the extent to which domestic wastewater is treated at municipal WWT plants in developed countries (UNEP, 1990). The information in Table 16 is somewhat dated and may not reflect the current status of WWT in Europe. Under pressure of European Union regulations, countries with bad WWT track records have started campaigns to improve the state of their WWT. In addition, countries in Southern Europe such as Spain, Greece, and Turkey have been spurred to improve the status of local WWT due to economic pressure from the tourist industry. For example, for many decades Spanish effluent received only rudimentary treatment before being discharged into rivers and seas; in 1990, only 40 percent of Spanish wastewater was treated. Under pressure to meet European Union regulations (90 percent reduction of load), Spain has begun a rigorous program to improve its track record and all over the country activated sludge WWT projects are now being initiated. Two plants under construction in Zaragossa and Ibiza will be furnished with a full cover to minimize air emissions. [World Water and Environmental Engineering (WWEE), 1992.]

If treated, domestic sewage may be treated in one or more lagoons, or at conventional (aerated activated sludge) WWT plants. Lagoons can be found in most regions of the world, however, lack of available land for the lagoon itself, as well as for the application of effluent, impedes their utilization. This is the case in densely populated parts of Asia (Doppenberg, 1994). The successful employment of partially aerated lagoons to serve small communities is reported from Thailand (Koottatep et al., 1994). The expansive use of lagoons is also reported from Latin America, the United States, Canada, Africa, and Europe, with the exception of the United Kingdom (Wiegant and Kalker, 1994; Racault, 1994; Evans et al., 1993; Doppenberg, 1994). There are approximately 2,000 lagoons in France and 1,000 in Germany and one third of all POTWs in the USA only use lagoons, as compared to activated sludge (Mara et al., 1992).

TABLE 16. POPULATION SERVED BY WWT IN DEVELOPED COUNTRIES

	PERCENT OF POPULATION SERVED.		
	Total	Served by Primary WWT only	Served by Primary and Secondary WWT
Austria	67	5	62
Belgium (1979)	23	no data	23
Canada	62	15	47
Denmark	98	8	90
Finland	74	0	74
France (1984)	50	no data	59
Germany (BRD) (1983)	87	8	79
Greece (1985)	1	no data	1
Ireland (1980)	11	no data	11
Italy (1980)	30	no data	no data
Japan	39	no data	no data
Luxembourg (1985)	83	14	69
Netherlands	90	7	83
New Zealand (1985)	88	8	85
Norway	43	6	37
Portugal	12	4	8
Spain (1985)	29	13	16
Sweden	100	1	99
Switzerland	85	no data	85
Turkey (1985)	4	2	2
Turkey (1993), (small towns)*	26	no data	no data
United Kingdom	84	6	78
United States (1984)	74	15	59

1987 data, unless otherwise indicated.
This table does not include treatment by septic sewage systems.
* From Sarikaya and Eroglu (1993).

In spite of the relative abundance of lagoons in different areas of the world, these lagoons have limited capacities and usually only serve small communities with no more than a few thousand inhabitants. For example, the Province of Ontario, Canada is reported to have 512 domestic WWT plants, 137 of which consist of lagoons. The lagoon plants serve small populations of 100 to 3,000 (Evans et al., 1993). If we assume that all

lagoon plants serve communities with the maximum reported number of 3,000 residents, these lagoon plants only serve 5 percent of the Ontario population. Domestic WWT by lagoons is considered a simple technology most suitable for small scale applications. For large scale domestic WWT applications, it is expected that aerated systems will be preferred over facultative lagoons because these systems have a larger capacity and use up less land space.

When assessing the extent of treatment it is important to take into consideration that in many countries conventional (aerated) WWT plants are not working properly (Mancy, 1993). In Eastern Europe, civil engineering development was arrested 40 years ago and as a result, there are many antiquated WWT plants, most of which are not running (Draaijer, 1994). A survey of 223 municipal WWT plants in Mexico (installed capacity equal to 15 percent of total sewage outflow) revealed that 45 percent of the plants were out of service and 35 percent suffered severe operational problems (Bartone, 1990). In Algeria, a World Bank study showed that 33 out of 42 plants were out of service. Experience in Korea with night soil treatment plants has been similar with respect to operational difficulties (Bartone, 1990). Lagoons also may be prone to operational failure, for example, they may receive loads that are too high in BOD and turn anaerobic. Such lagoons and ill managed or overloaded municipal WWT plants are expected to be a source of CH_4 and possibly other GHG emissions.

Available country-specific information on BOD and COD loadings, and the assumed type and extent of treatment are summarized in Table 17. The methodology for calculating CH_4 emissions from domestic wastewater used in this report, as adapted from Equation 10, is presented in the next chapter in combination with emission estimates.

TABLE 17. COUNTRY-SPECIFIC DOMESTIC WASTEWATER DATA

Country	Population	To City Sewer	Land	Septic Tank, Latrine	Raw Discharge	To WWTP	Anaer-obic WWT	Aerobic WWT	TA_c*
	(10^6)	(%)	(%)	(%)	(%)	(%)	(%)		(%)
AFRICA									
Nigeria	127	10	50	40	90	10	50	50	0.5
Egypt	59	10	50	40	80	20	50	50	1.0
Kenya	28	10	50	40	60	40	50	50	2.0
South Africa	43	40	30	30	60	40	20	80	3.2
Zimbabwe	12	40	30	30	60	40	20	80	3.2
Other Africa	492	10	50	40	90	10	50	50	0.5
ASIA									
China	1,238	15	20	65	90	10	50	50	0.8
India	931	15	50	35	90	10	50	50	0.8
Indonesia	201	15	40	45	80	20	50	50	1.5
Pakistan	135	15	50	35	90	10	50	50	0.8
Bangladesh	128	15	50	35	90	10	50	50	0.8
Japan	126	90	0	10	10	90	5	95	4.1
Other Asia	726	15	20	65	90	10	50	50	0.8
EUROPE									
Russia	150	70	0	30	50	50	40	60	14.0
Germany	81	80	0	20	0	100	5	95	4.0
United Kingdom	58	90	0	10	0	100	5	95	4.5
France	58	80	0	20	5	95	5	95	3.8
Italy	58	80	0	20	10	90	5	95	3.6
Other OECD	113	70	0	30	25	75	5	95	2.6
Other Europe	217	70	0	30	50	50	10	90	3.5
NORTH AMERICA									
United States	263	70	0	30	0	100	5	95	3.5
Canada	29	70	0	30	0	100	5	95	3.5
LATIN AMERICA AND CARIBBEAN									
Brazil	161	40	40	20	95	5	50	50	1.0
Mexico	94	40	40	20	95	5	50	50	1.0
Others	224	40	40	20	95	5	50	50	1.0
AUSTRALIA AND NEW ZEALAND									
Australia	18	70	5	25	5	95	5	95	3.3

Notes: WWTP = Wastewater treatment plant
TA_c = Country-specific fraction of COD that is treated anaerobically
* Assume a margin of error of a factor of 2 (i.e., -50%, +100%)

References for Africa: Bartone, 90; Draaijer, 94; WHO/UNICEF, 93; Doppenberg 94; Marks, 93; Alabaster, 91.
References for Asia: Bartone, 90; Draaijer, 94; WHO/UNICEF, 93; Doppenberg 94; Koottatep, 94; UNEP, 90.
References for Europe: Doppenberg, 94; UNEP, 90; Draaijer 94; WWEE, 92; Racault, 94; Mara et al., 92.
References for North America: Evans et al., 93; UNEP, 90.
References for Australia and New Zealand: WHO/UNICEF, 93; Jordao and Leitao, 90; UNEP, 90.

ESTIMATES OF GHG EMISSIONS FROM WWT

METHANE

Industrial Wastewater

The generic methodology in Equation 10 was modified to develop emissions estimates for CH_4 from industrial wastewater. Equation 11 provides the methodology for estimating CH_4 from industrial wastewater.

$$CH_4 \text{ emissions} = EF * 10^{-12} * \sum_i \sum_c (P_{ic} * Q_i * COD_i * TA_{ic}) \quad (Tg/yr) \qquad (11)$$

where:
- EF = Emission factor (g CH_4/g $COD_{removed}$);
- P_{ic} = Industry- and country-specific product output (Mg/yr);
- Q_i = Industry-specific wastewater produced per unit of product (m^3/Mg);
- COD_i = Organics loading removed, by industry (g/m^3);
- TA_{ic} = Industry- and country-specific fraction of COD in wastewater treated anaerobically;
- Subscript i = An individual industry; and
- Subscript c = An individual country.

For each industry group, the countries with the highest product outputs were identified and all other remaining countries were grouped "Rest of the World" (see Table 18). Outputs P_{ic} were taken from the UNISY data base. Table 18 includes industry-specific wastewater generation rates Q_i and average, industry-specific COD data, which came from Table 12. Country-specific data for Q_i and COD_i were not available. TA_{ic}, the industry- and country-specific fractions of COD in the wastewater that is expected to be treated anaerobically, were retrieved from Table 13. The product of the aforementioned parameters representing the amount of the COD in the wastewater that is expected to be treated anaerobically was multiplied by the emission factor of 0.3 ± 0.1 g CH_4/g COD.

Based on the information in Table 18, 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. According to Table 18, the biggest contributor to industrial CH_4 emissions from WWT is the pulp and paper industry (see Figure 3). Although pulp and paper wastewater is typically treated aerobically, it was assumed that up to 15 percent of the COD in treated pulp and paper wastewater in developing and Eastern European countries may degrade under anaerobic conditions as a result of poor wastewater management.

TABLE 18. COUNTRY-SPECIFIC INDUSTRIAL WASTEWATER DATA AND METHANE EMISSIONS

INDUSTRY TYPE	COUNTRY	Output	Wastewater Generation		COD			Total COD	TA_{ic}	COD Anaer.	COD to City Sewers		Methane Emissions		
		(Tg/yr)	(m^3/Mg)	(10^9 l/yr)	(g/l)			(Tg/yr)	(%)	(Tg/yr)	(%)	(Tg/yr)	(Gg/yr)		
					low	mean	high						low	mean	high
Group 1. Animal Products															
Meat & Poultry	United States	28.59	13	372	2	4.1	7	1.5	77	1.17	15	0.2	114	352	801
Meat & Poultry	Germany	6.74	13	88	2	4.1	7	0.4	72	0.26	20	0.1	25	78	177
Meat & Poultry	Russia	6.64	13	86	2	4.1	7	0.4	23	0.08	25	0.1	8	24	56
Meat & Poultry	Brazil	5	13	68	2	4.1	7	0.3	32	0.09	15	0.0	9	27	61
Meat & Poultry	United Kingdom	4.17	13	54	2	4.1	7	0.2	72	0.16	20	0.0	16	48	109
Meat & Poultry	Japan	3.53	13	46	2	4.1	7	0.2	65	0.12	18	0.0	12	37	84
Meat & Poultry	Ukraine	3.01	13	39	2	4.1	7	0.2	23	0.04	25	0.0	4	11	25
Meat & Poultry	Rest of the world	17.2	13	224	2	4.1	7	0.9	35	0.32	12	0.1	31	96	219
Dairy Products	United States	6.46	7	45	1.5	2.7	5.2	0.1	77	0.09	15	0.0	10	28	72
Dairy Products	France	4.97	7	35	1.5	2.7	5.2	0.1	72	0.07	20	0.0	8	20	52
Dairy Products	Germany	3.71	7	26	1.5	2.7	5.2	0.1	72	0.05	20	0.0	6	15	39
Dairy Products	Russia	2.41	7	17	1.5	2.7	5.2	0.0	23	0.01	25	0.0	1	3	8
Dairy Products	Rest of the world	14.6	7	102	1.5	2.7	5.2	0.3	35	0.10	12	0.0	11	29	74
Fish Processing	Japan	5.39	13	70	1.25	2.5	5	0.2	10	0.02	18	0.0	2	5	14
Fish Processing	Rest of the world	12.5	13	163	1.25	2.5	5	0.4	35	0.14	12	0.0	14	43	114
Group 2. Industrial Plant Processing															
Alcohol Refining	Brazil	11.78	24	283	5	11	22	3.1	13	0.40	24	0.7	37	121	324
Alcohol Refining	United States	3.11	24	75	5	11	22	0.8	8	0.07	20	0.2	6	20	53
Alcohol Refining	Rest of the world	16	24	386	5	11	22	4.3	11	0.47	10	0.4	43	140	374
Wine & Vinegar	France	6.55	23	151	0.7	1.5	3	0.2	4	0.01	60	0.1	1	3	7
Wine & Vinegar	Italy	5.49	23	126	0.7	1.5	3	0.2	4	0.01	60	0.1	1	2	6
Wine & Vinegar	Spain	2.34	23	54	0.7	1.5	3	0.1	4	0.00	54	0.0	0	1	3
Wine & Vinegar	Rest of the world	14	23	327	0.7	1.5	3	0.5	11	0.05	10	0.0	5	16	43
Vegetable Oils	United States	6.76	3.1	21	0.5	0.9	1.2	0.0	8	0.00	20	0.0	0	0	1
Vegetable Oils	Malaysia	6.14	3.1	19	0.5	0.9	1.2	0.0	11	0.00	2	0.0	0	1	1
Vegetable Oils	China	5.44	3.1	17	0.5	0.9	1.2	0.0	11	0.00	2	0.0	0	1	1
Vegetable Oils	Brazil	4.12	3.1	13	0.5	0.9	1.2	0.0	13	0.00	24	0.0	0	0	1
Vegetable Oils	Rest of the world	35	3.1	108	0.5	0.9	1.2	0.1	11	0.01	10	0.0	1	3	6
Sugar Refining	India	23.31	9	210	1	3.2	6	0.7	11	0.07	2	0.0	5	22	55

TABLE 18 (continued)

INDUSTRY TYPE	COUNTRY	Output	Wastewater Generation		COD			Total COD	TA_{ic}	COD Anaer.	COD to City Sewers		Methane Emissions		
		(Tg/yr)	(m^3/Mg)	(10^9 l/yr)	(g/l)			(Tg/yr)	(%)	(Tg/yr)	(%)	(Tg/yr)	(Gg/yr)		
					low	mean	high						low	mean	high
Sugar Refining	Ukraine	12.18	9	110	1	3.2	6	0.4	8	0.03	25	0.1	2	8	21
Sugar Refining	Brazil	10.15	9	91	1	3.2	6	0.3	13	0.04	24	0.1	2	11	29
Sugar Refining	Cuba	8.05	9	72	1	3.2	6	0.2	13	0.03	24	0.1	2	9	23
Sugar Refining	United States	6.27	9	56	1	3.2	6	0.2	8	0.01	20	0.0	1	4	11
Sugar Refining	Rest of the world	87	9	785	1	3.2	6	2.5	11	0.28	10	0.3	17	83	207
Malt & Beer	United States	25.89	6.3	163	2	2.9	7	0.5	8	0.04	20	0.1	5	11	37
Malt & Beer	Germany	13.01	6.3	82	2	2.9	7	0.2	4	0.01	60	0.1	1	3	9
Malt & Beer	Indonesia	11.29	6.3	71	2	2.9	7	0.2	11	0.02	2	0.0	3	7	22
Malt & Beer	United Kingdom	8.29	6.3	52	2	2.9	7	0.2	4	0.01	60	0.1	1	2	6
Malt & Beer	China	6.92	6.3	44	2	2.9	7	0.1	11	0.01	2	0.0	2	4	13
Malt & Beer	Japan	6.71	6.3	42	2	2.9	7	0.1	8	0.01	19	0.0	1	3	9
Malt & Beer	Rest of the world	62	6.3	391	2	2.9	7	1.1	11	0.12	10	0.1	17	37	120
Starch Production	United States	11	9	99	1.5	10	42	1.0	8	0.08	20	0.2	2	24	133
Starch Production	Europe	8.5	9	77	1.5	10	42	0.8	8	0.06	50	0.4	2	18	103
Starch Production	Rest of the world	10.5	9	95	1.5	10	42	0.9	11	0.10	10	0.1	3	31	175
Group 3. Vegetables, Fruits, and Textiles															
Veg., Fruits, & Juices	United States	8.68	20	174	2	5	10	0.9	0	0.00	95	0.8	0	0	0
Veg., Fruits, & Juices	Germany	4	20	80	2	5	10	0.4	0	0.00	95	0.4	0	0	0
Veg., Fruits, & Juices	Rest of the world	18.7	20	374	2	5	10	1.9	4	0.07	30	0.6	6	22	60
Textiles (natural)	China	9.73	172	1,673	0.8	0.9	1.6	1.5	3	0.05	4	0.1	8	14	32
Textiles (natural)	United States	4.4	172	756	0.8	0.9	1.6	0.7	0	0.00	95	0.6	0	0	0
Textiles (natural)	India	3.32	172	571	0.8	0.9	1.6	0.5	3	0.02	4	0.0	3	5	11
Textiles (natural)	Rest of the world	15.9	172	2,735	0.8	0.9	1.6	2.5	4	0.10	30	0.7	18	30	70
Soft drinks	Indonesia	24.48	2	49	1	2	4	0.1	3	0.00	4	0.0	0	1	2
Soft drinks	United States	15	2	30	1	2	4	0.1	0	0.00	95	0.1	0	0	0
Soft drinks	Rest of the world	63.9	2	128	1	2	4	0.3	4	0.01	30	0.1	1	3	8
Group 4. Pulp & Paper															
Pulp & Paper	Canada	9.07	162	1,469	1	8.5	15	12.5	1	0.12	0	0.0	3	37	88
Pulp & Paper	United States	6	162	972	1	8.5	15	8.3	1	0.08	0	0.0	2	25	58
Pulp & Paper	Japan	3.5	162	567	1	8.5	15	4.8	1	0.05	0	0.0	1	14	34
Pulp & Paper	Rest of the world	13.4	162	2,171	1	8.5	15	18.5	12	2.21	0	0.0	52	664	1,563

TABLE 18 (continued)

INDUSTRY TYPE	COUNTRY	Output	Wastewater Generation		COD			Total COD	TA_{ic}	COD Anaer.	COD to City Sewers		Methane Emissions		
		(Tg/yr)	(m^3/Mg)	(10^9 l/yr)	(g/l)			(Tg/yr)	(%)	(Tg/yr)	(%)	(Tg/yr)	(Gg/yr)		
					low	mean	high						low	mean	high
Group 5. Organic Chemicals and Related Products															
Organic Chemicals	France	15.6	67	1,045	0.8	3	5	3.1	3	0.09	30	0.9	5	28	63
Organic Chemicals	Germany	14.84	67	994	0.8	3	5	3.0	3	0.09	30	0.9	5	27	60
Organic Chemicals	India	11.24	67	753	0.8	3	5	2.3	4	0.09	4	0.1	5	27	60
Organic Chemicals.	Japan	26.65	67	1,786	0.8	3	5	5.4	3	0.16	27	1.4	9	48	107
Organic Chemicals	United States	101	67	6,767	0.8	3	5	20.3	1	0.20	20	4.1	11	61	135
Organic Chemicals	Rest of the world	60	67	4,020	0.8	3	5	12.1	3	0.36	10	1.2	19	109	241
Soap & Detergents	China	2.58	3.1	8	0.5	0.9	1.2	0.0	4	0.00	4	0.0	0	0	0
Soap & Detergents	United States	3.87	3.1	12	0.5	0.9	1.2	0.0	1	0.00	20	0.0	0	0	0
Soap & Detergents	Rest of the world	26	3.1	81	0.5	0.9	1.2	0.1	3	0.00	10	0.0	0	1	1
Paints	United States	4.18	0.6	2.5	1	5.1	10	0.0	1	0.00	20	0.0	0	0	0
Paints	Indonesia	6.38	0.6	3.8	1	5.1	10	0.0	4	0.00	4	0.0	0	0	1
Paints	Rest of the world	14.3	0.6	8.6	1	5.1	10	0.0	3	0.00	10	0.0	0	0	1
Petroleum Refineries	United States	715	0.6	429	0.4	1	1.6	0.4	1	0.00	20	0.1	0	1	3
Petroleum Refineries	Rest of the world	1,435	0.6	861	0.4	1	1.6	0.9	3	0.03	10	0.1	2	8	17
Plastics and Resins	Germany	16.33	67	1,094	0.4	1	1.6	1.1	3	0.03	30	0.3	3	10	21
Plastics and Resins	Japan	13.55	67	908	0.4	1	1.6	0.9	3	0.03	27	0.2	2	8	17
Plastics and Resins	United States	24.28	67	1,627	0.4	1	1.6	1.6	1	0.02	20	0.3	1	5	10
Plastics and Resins	Rest of the world	54	67	3,618	0.4	1	1.6	3.6	3	0.11	10	0.4	9	33	69
Coke	United States	21	0.8	17	0.05	0.1	0.2	0.0	1	0.00	20	0.0	0	0	0
Coke	World	243	0.8	194	0.05	0.1	0.2	0.0	3	0.00	10	0.0	0	0	0
Total Global (Tg/yr):								**131**		**8.6**		**18**	**0.6**	**2.6**	**6.4**

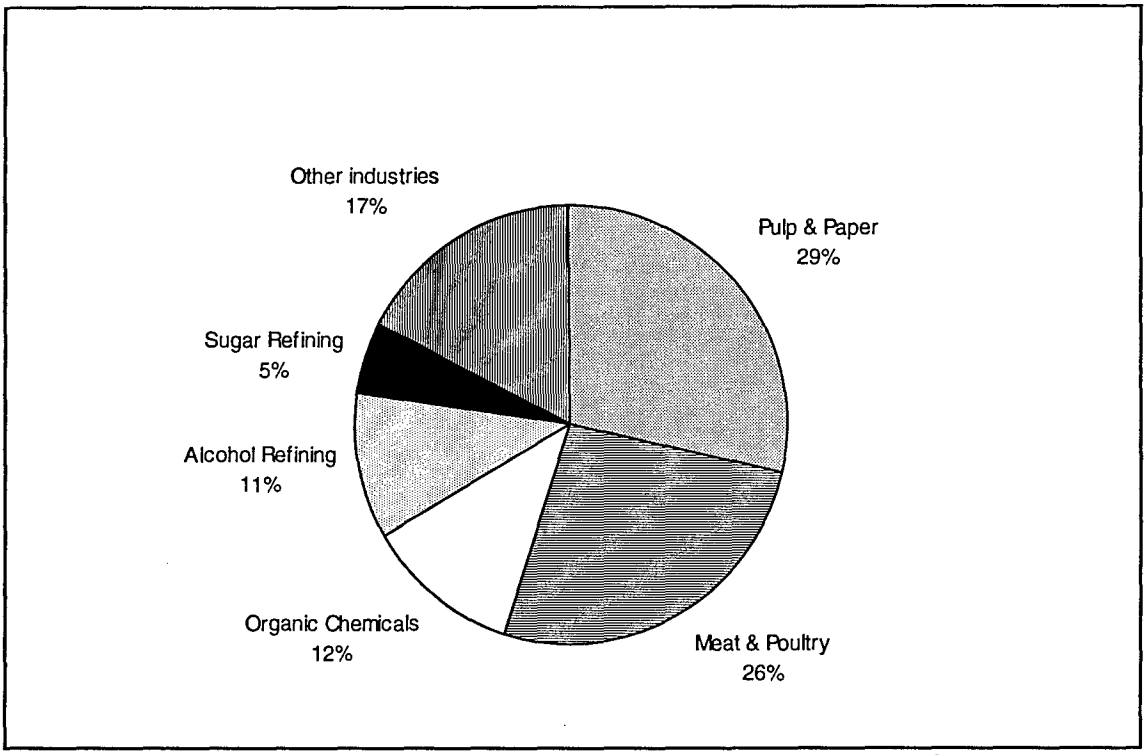

Figure 3. World Methane Emissions from Anaerobic Industrial WWT.

The second principal contributor to CH_4 emissions from WWT is the meat and poultry industry which is known to use anaerobic lagoons. Also, the alcohol, sugar refining industries, and organic chemicals manufacturing are major contributors to CH_4 emissions from WWT. Again, it was assumed that for these industries some anaerobic WWT conditions may occur resulting in CH_4 emissions.

Earlier estimates for global CH_4 emissions from industrial WWT are significantly higher [i.e., between 26 and 40 Tg/yr (U.S. EPA, 1994)]. The two main reasons that the emissions in this current report are lower are that iron and steel manufacturing and petroleum refining are excluded as significant categories and that the fraction of wastewater degrading anaerobically is significantly lower for most remaining categories. (In U.S. EPA 1994, it was assumed that between 10 and 15 percent of wastewater degrades anaerobically.)

Domestic Wastewater

The methodology for calculating CH_4 emissions from domestic wastewater used in this report is represented by Equation 12, adapted from Equation 10.

$$CH_4 \text{ emissions} = EF * 10^{-12} * \sum_c (P_c * COD_c * 365 * TA_c) \quad (Tg/yr) \qquad (12)$$

where: EF = Emission factor (g CH_4/g $COD_{removed}$);
P_c = Country population;
COD_c = Country-specific per capita COD generation (g/day);
TA_c = Country-specific fraction of COD treated anaerobically; and
Subscript c = An individual country.

Country populations P are readily available in the literature and region-specific per capita COD generation rates come from Table 15. Country-specific COD loadings in domestic wastewater and information on the country-specific fraction of COD that is treated anaerobically (TA_c) is included in Table 19. TA_c does not only represent anaerobic lagoons; WWT plants that are predominantly aerobic may have an anaerobic primary treatment step. Also, certain pockets of the aerobic WWT process (e.g., holding tanks or maturation ponds may be intentionally, or unintentionally anaerobic and in addition there may be on-site sludge storage or holding under anaerobic conditions). As previously mentioned, actual sludge treatment is excluded from this research.

The product of the aforementioned parameters representing the amount of the COD in the wastewater that is expected to be treated anaerobically was multiplied by the emission factor of 0.3 ± 0.1 g CH_4/g COD. Table 19 includes estimates of the amount of CH_4 that is emitted from anaerobic domestic WWT for different regions of the world. According to Table 19, 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 contribute. The country is expected to have an advanced sewer line network, but lacks the financial and technical means to perform proper WWT. This situation is expected to result in anaerobic conditions. Earlier estimates for global CH_4 emissions from domestic WWT are 2.3 Tg/yr (U.S. EPA, 1994).

Industrial Wastewater Discharged into Sewers

Equation 11 was adapted to obtain an estimate of global CH_4 emissions from industrial wastewater that is discharged into municipal sewers to be treated at municipal WWT plants.

$$CH_4 \text{ emissions} = EF * COD_{total} * TA_{c,\ average} \quad (Tg/yr) \qquad (13)$$

where: EF = Emission factor (g CH_4/g $COD_{removed}$);
COD_{total} = Total COD (Tg/yr) discharged into municipal sewers;
TA_c = Country-specific fraction of COD that is treated anaerobically; and
Subscript c = An individual country.

Wastewater from this source category is likely to mix completely with domestic wastewater and will undergo the same transportation and degradation routes as domestic COD. Accordingly, TA_c for domestic wastewater may be used. The average global TA_c

TABLE 19. GLOBAL CH_4 EMISSIONS FROM ANAEROBIC DOMESTIC WASTEWATER TREATMENT

Country	Population	BOD	Total COD Generation[1]			TA_c	COD Treated (anaerobic)			CH_4 from Anaerobic Wastewater Treatment		
	(Million)	(g/capita/day)	(Tg/yr)			(%)	(Gg/yr)			(Gg/yr)		
			low	mean	high		low	mean	high	low	mean	high
AFRICA												
Nigeria	127	35+/-10	2.9	4.1	5.2	0.5	14	20	26	3	6	10
Egypt	59	35+/-10	1.3	1.9	2.4	1.0	13	19	24	3	6	10
Kenya	28	35+/-10	0.6	0.9	1.1	2.0	13	18	23	3	5	9
South Africa	43	40+/-10	1.2	1.6	2.0	3.2	37	50	62	7	15	25
Zimbabwe	12	40+/-10	0.3	0.4	0.5	3.2	10	13	17	2	4	7
Other Africa	492	35+/-10	11.2	15.7	20.2	0.5	56	79	101	11	24	40
ASIA												
China	1,238	35+/-10	28	40	51	0.8	212	297	381	42	89	153
India	931	35+/-10	21	30	38	0.8	159	223	287	32	67	115
Indonesia	201	35+/-10	4.6	6.4	8.3	1.5	69	97	124	14	29	50
Pakistan	135	35+/-10	3.1	4.3	5.5	0.8	23	32	42	5	10	17
Bangladesh	128	35+/-10	2.9	4.1	5.3	0.8	22	31	39	4	9	16
Japan	126	55+/-15	4.6	6.3	8.0	4.1	186	256	326	37	77	130
Other Asia	726	35+/-10	17	23	30	0.8	124	174	224	25	52	89
EUROPE												
Russia	150	50+/-10	4.8	6.8	8.9	14.0	670	956	1,243	134	287	497
Germany	81	60+/-15	3.3	4.4	5.6	4.0	133	178	222	27	53	89
United Kingdom	58	60+/-15	2.4	3.2	4.0	4.5	107	143	179	21	43	72
France	58	60+/-15	2.4	3.2	4.0	3.8	91	121	151	18	36	60
Italy	58	60+/-15	2.4	3.2	4.0	3.6	86	114	143	17	34	57
Other OECD	113	60+/-15	4.6	6.2	7.7	2.6	122	162	203	24	49	81
Other Europe	217	60+/-15	8.9	12	15	3.5	312	416	520	62	125	208
NORTH AMERICA												
United States	263	65+/-15	13	17	20	3.5	462	588	714	92	176	286
Canada	29	60+/-15	1.2	1.6	2.0	3.5	41	55	68	8	16	27
LATIN AMERICA AND CARIBBEAN												
Brazil	161	35+/-10	3.7	5.2	6.6	1.0	37	52	66	7	15	27
Mexico	94	35+/-10	2.1	3.0	3.8	1.0	21	30	38	4	9	15
Others	224	35+/-10	5.1	7.2	9.2	1.0	51	72	92	10	21	37
AUSTRALIA AND NEW ZEALAND												
Australia	18	60+/-15	0.7	1.0	1.2	3.5	26	34	43	5	10	17
Total Global (Tg/yr):			**154**	**212**	**270**		**3.1**	**4.2**	**5.4**	**0.6**	**1.3**	**2.1**

[1] A factor of 2.5 was used to convert BOD to COD.

from Table 17 is estimated to be about 4 percent and it is estimated that about 17.2 Tg/yr of industrial COD is discharged into municipal sewers (see Table 18). As with other industrial and domestic wastewater, the emission factor (0.3 g CH_4/g COD). CH_4 emissions from industrial wastewater that is treated at municipal WWT plants are estimated to be 0.2 Tg/yr.[11]

CARBON DIOXIDE

The field test report (Eklund and LaCosse, 1997) concludes that facultative lagoons that treat municipal wastewater are not a significant source of any GHGs, with the possible exception of CO_2. The report mentions that OPM/FTIR results were not conclusive for CO_2 emissions from anaerobic lagoons. No other emissions information on CO_2 emissions from WWT was found and Table 15 contains no CO_2 emission factors, other than the theoretical emission factor which was based on a stoichiometrical mass balance calculation (i.e., 1.37 g CO_2/g COD) (pp. 12 and 13).

The theoretical emission factor can be used to develop an estimate of maximum CO_2 emissions by assuming that all COD in wastewater decomposes aerobically. The total amount of COD generated from industrial and domestic sources is estimated to be about 343 Tg/yr (see Table 18 and 19), and total global CO_2 emissions from industrial and domestic wastewater combined are estimated to be 470 Tg/yr. Human wastewater generation is the single largest source (290 Tg/yr). The global pulp and paper, and organic chemicals manufacturing industries account for 69 percent of CO_2 emissions from all industrial sources. As a comparison, CO_2 emissions from U.S. fossil fuel combustion are estimated to be 5,000 Tg/yr (U.S. EPA, 1993b).

NITROUS OXIDE

N_2O emissions from WWT can be associated with the anaerobic or anoxic decomposition of organic matter containing proteins and other organic nitrogen compounds (page 27). The following emission factors were suggested to estimate N_2O emissions from WWT: 5.1 g/capita/yr for conventional[12] domestic WWT; and 0.09 g/g COD for anaerobic WWT that is either domestic or industrial. Aerobic industrial WWT may also have denitrification, but currently no emission factor exists for this source category.

By using data from Table 17 it was estimated that 734 million people in the world are served by conventional WWT including aerobic and facultative lagoons. Consequently, global N_2O emissions from conventional domestic WWT are estimated at 5.1 × 734 = 3,743 Mg/yr (0.004 Tg/yr).

Estimated global N_2O emissions from anaerobic domestic WWT are 0.09 × 5.4 = 0.5 Tg N_2O/yr. The amount of COD in global domestic wastewater that is treated under

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[11] This does not include emissions for untreated industrial wastewater in sewers or gutters.

[12] Most conventional WWT is expected to be activated sludge WWT with nitrification/denitrification.

anaerobic conditions is 5.4 Tg/yr (Table 19). For the United States, it was estimated that 4 percent of COD in domestic wastewater is treated under anaerobic conditions which is equivalent to 0.59 Tg/yr (Tables 17 and 18). Thus, U.S. N_2O emissions from anaerobic domestic WWT can be estimated at 0.05 Tg/yr. These estimates are coarse estimates and are provided only to illustrate the potential significance of the source categories. They do not include potential emissions from other anaerobic domestic wastewater sources, such as septic tanks, latrines, and possibly certain sewers that may have anaerobic sections.

Wastewater from the meat, poultry, fish, and dairy processing industries is expected to contain substantial amounts of bound nitrogen. According to Table 18, the amount of COD in anaerobic wastewater from these industries is estimated to be 2.7 Tg/yr. Consequently, global N_2O emissions from this source category are estimated at $0.09 \times 2.7 = 0.24$ Tg N_2O per year. For the United States, the amount of COD from this source category is estimated at 1.3 Tg/yr, resulting in estimated emissions of 0.12 Tg N_2O/yr. As a comparison, current U.S. estimates for total N_2O emissions are 0.4 Tg/yr and do not include WWT. These estimates are associated with large uncertainties and are, at best, an indication of the relative significance of this source category.

Some other absolute and relative estimates were found in the literature. Czepiel et al. (1995) estimated that for the United States N_2O emissions from conventional activated sludge WWT were 1,200 Mg/yr or 0.3 percent of national emissions. Schön et al., (1993) estimated that German N_2O emissions from activated sludge WWT are about 850 Mg/yr or 0.2 percent of total German N_2O emissions. Debruyn et al., (1994) estimated that N_2O emissions from Belgian wastewater are 0.6 percent of total Belgian emissions, but provides no absolute figures. As the emission factor for conventional WWT that was used in this report is based on data from the aforementioned authors, no relative U.S. data are provided. The combined N_2O emission estimates from anaerobic industrial and domestic WWT, based on the emission factor from the field tests are 0.17 Tg/yr.

TABLE 20. SUMMARY OF GLOBAL GHG ESTIMATES FOR DOMESTIC AND INDUSTRIAL WWT.

GHG	SOURCE	LOWER BOUND (Tg/yr)	AVERAGE (Tg/yr)	UPPER BOUND (Tg/yr)	REMARKS
CH_4	Industrial WWT	0.6	2.4	6.1	
CH_4	Domestic WWT	0.6	1.3	2.1	
N_2O	Domestic Activated Sludge WWT		0.004		These are rough estimates. No lower and upper bounds are available.
N_2O	Domestic Anaerobic WWT		0.5		
N_2O	Anaerobic WWT at meat, poultry, fish, and dairy processing industries		0.24		

UNCERTAINTIES

Uncertainties Associated With the CH_4 Emission Factor

The specific uncertainties associated with the development of the field test emission factors, such as the representativeness of the test sites and suitability of the test procedures, are discussed in the field test report (Eklund and LaCosse, 1997). It is believed that the field test emission factors reflect an upper-end estimate because part of the CH_4 may not come from the wastewater but from sludge at the bottom of the lagoons that had been deposited in previous years (see Appendix C).

The CH_4 emission factor used in this report is expressed as 0.3 ± 0.1 g CH_4/g $COD_{removed}$. The emission factor reflects a value that is based on theoretical and digester data, as well as, the lower-end of the range of the emission factors derived from the field test results. The emission factor expresses CH_4 emissions per mass of $COD_{removed}$ and is used for all types of organic wastewater. $COD_{removed}$ is a surrogate for the amount of degradable organic carbon in the wastewater that can be turned into CH_4. The ratio of COD to actual degradable organic carbon may vary for different types of wastewater. Inorganic components in wastewater will also contribute to the COD. As this report only examines wastewater that is basically organic in nature, errors associated with inorganic COD cannot be examined but are thought to be relatively minor. Nevertheless, the correlation between COD and emissions of specific GHGs warrants more research.

The range for the emission factor (i.e., ± 0.1 g CH_4/g $COD_{removed}$) is based on expert judgement and accounts for the aforementioned uncertainties associated with the use of COD and the extrapolation to different types of wastewater. This emission factor is believed to be conservative (i.e., on the high side). The reason is that both the theoretical and digester emission factors reflect upper-end estimates. Also, the field test emission factors reflect emissions that may be relatively high.

Uncertainties Associated With Industrial Wastewater Activity Data

Equation 11 expresses the methodology used to estimate emissions from industrial wastewater. The uncertainties associated with each activity parameter in the equation are addressed below.

Country-specific annual industrial output data (P_{ic}) are compiled by the United Nations and published in the Industrial Statistical Yearbook or UNISY. P_{ic} numbers were multiplied by average industry-specific wastewater outflow (Q_i in m^3/Mg of product) and COD_i values (g/l) to obtain total COD in wastewater (Tg/yr). The UNISY data base contains over 100 countries and includes output data for each country for up to 22 industrial categories. It may be presumed that some reporting errors are made and the data reduction that was necessary to make the data base manageable may also have lead to inaccuracy. Compared to the uncertainties that are expected to be associated with average Q_i and COD_i values, uncertainties in P_{ic} are expected to be relatively minor.

Q_i and COD_i values depend on the product that is being produced, the production process, and the efficiency of the process. The type and efficiency of the industrial process

are likely to be dependent on plant scale, availability and cost of water, local water and wastewater regulations and the degree of enforcement. Ultimately, it is expected that errors are associated with the extrapolation of data across industries, even within the same category. It is likely that there is a certain inverse correlation between Q_i and COD_i, and possibly P_i.[13] Because of this likely correlation, it was decided to assign ranges to reflect the inaccuracies of the total COD numbers and not to the individual constituents P_{ic}, Q_i, and COD_i. Table 12 includes average Q_i and COD_i values, as well as ranges for Q_i and COD_i. If only one data set was available, the range was assumed to be a factor of two (i.e., 50 percent, +100 percent). For most industries, the variability in COD_i values are considerably wider than the ranges for Q_i. Therefore, the ranges in COD_i values were also used to reflect the uncertainty in the total COD output.

Assignment of values for the industry- and country-specific fraction of COD in wastewater that is treated anaerobically at the industrial site (TA_{ic}) is based on anecdotal information and on engineering judgement. Anecdotal information addresses the limited degree of WWT in many parts of the world. Engineering judgement includes knowledge on restrictions in aerobic or anaerobic WWT for certain industries.

Apart from treatment of meat and poultry processing wastewater, anaerobic treatment is uncommon. Nevertheless, average values for TA_{ic} in Table 13 are higher than zero. For OECD countries, TA_{ic} values are typically between 1 and 4 percent, and for developing and Eastern European countries TA_{ic} values may be as high as 20 percent (e.g., the Russian pulp and paper industry). For OECD countries it was assumed that some anaerobic conditions may exist, for instance as a result of poorly aerated sections of lagoons or tertiary sedimentation basins. Also, temporary sludge storage on site may be a source of CH_4 emissions. For developing and Eastern European countries the same assumptions were made, but it also was assumed that under-aeration and/or overloading of aerobic WWT system may easily result in anaerobic conditions. Significant uncertainties are associated with these assumptions.

A sensitivity analysis was conducted to quantify and compare the uncertainties associated with the different parameters used to develop CH_4 emissions from industrial WWT. Different parameters were varied and the percent change in total global CH_4 emissions was recorded. As pulp and paper, meat and poultry, organic chemicals, and alcohol and starch are expected to be the prime sources for CH_4 emissions from industrial WWT, the sensitivity analysis is limited to these groups.

As is indicated by Table 21, relatively large uncertainties are associated with the quantification of the degree of wastewater that may decompose under anaerobic conditions in WWT plants that are designed to be aerobic.

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[13] This correlation is based on economies of scale and on the understanding that the wastewater stream is an indicator of process efficiency. For a large plant, the combination of per unit wastewater outflow and wastewater loading is likely to be lower than for a smaller plant. A certain plant may have a relatively small flow of highly concentrated wastewater or it may have a relatively larger flow of diluted wastewater.

TABLE 21. SENSITIVITY ANALYSIS OF INDUSTRIAL CH_4 ESTIMATES

INDUSTRY GROUP	OLD ASSUMPTION (STATUS QUO)	NEW ASSUMPTION	CHANGE IN GLOBAL CH_4 EMISSIONS
Pulp and Paper	Some anaerobic decomposition likely (e.g., overloading, underaeration)	WWT is 100% aerobic	-27%
Pulp and Paper	WWT in OECD countries is 1% anaerobic	WWT in OECD countries is 4% anaerobic	+ 8%
Organic Chemicals, et al.	Raw discharge in developing countries is 60% and in OECD countries 0 to 10%	Raw discharge more widespread: 80% in developing countries. 10% in OECD countries.	-3%
Organic Chemicals, et al.	Treatment on site is 50 to 90%	Treatment on site is 25 to 45%	-7%
Organic Chemicals, et al., and Alcohol and Sugar Refining	Some anaerobic decomposition likely (e.g., overloading, underaeration, sludge storage)	Anaerobic WWT/decomposition is twice of what was assumed before.	+ 17%
Meat and Poultry	70 to 95% of wastewater assumed to be treated on site.	100% of wastewater is treated on site (as opposed to some discharge into sewers)	+ 5%

Uncertainties Associated With Domestic Wastewater Activity Data

The emission factor used for estimating CH_4 emission from anaerobic domestic WWT is the same as for industrial wastewater. Uncertainties associated with the emission factor are discussed there. The country populations are believed to be relatively accurate and no ranges were defined for this parameter. Country-specific per capita COD generation rates (g/day) are also believed to be well known. Values and ranges are included in Table 15. These ranges are propagated in the ultimate emission estimates.

Table 17 includes information on the country-specific fraction of COD that is treated anaerobically (TA_c). Assumptions were made to quantify the extent to which sewage is discharged into a city sewer to be treated at a municipal WWT plant. Only for OECD countries is domestic sewage typically treated at municipal WWT plants, whereas for other countries sewage is mostly discharged without treatment or treated in latrines. (Latrines and septic tanks as a source for GHG emissions are not included in this research.) In OECD countries WWT is expected to be almost fully aerobic (90 to 95 percent). The remaining 5 to 10 percent reflect probable anaerobic conditions in sections of the process, such as sedimentation tanks, and sludge storage. For other countries it was assumed that 50 percent of WWT is anaerobic. This number reflects the use of anaerobic lagoons, as well as, mismanagement or overloading of aerobic systems and/or facultative lagoons.

Compared to industrial WWT, the uncertainties associated with the extent of domestic WWT are not expected to be as large. More information is available in the literature, for example on sanitation issues, and this information can also be used to define the extent of sewerage and types of WWT. Table 22 includes a sensitivity analysis to quantify and compare the uncertainties associated with TA_c. Different components of TA_c were varied and the percent change in total global CH_4 emissions was recorded.

TABLE 22. SENSITIVITY ANALYSIS OF DOMESTIC CH_4 ESTIMATES

OLD ASSUMPTION (STATUS QUO)	*NEW ASSUMPTION*	*CHANGE IN GLOBAL CH_4 EMISSIONS*
In developing countries about 50% of WWT is anaerobic.	In developing countries about 25% of WWT is anaerobic. (Improve WWT plant management)	-30%
In developing countries there is little WWT	Amount of WWT is twice as high (see Table 17)	+ 69%
In developing countries 10 to 15% of population has a sewer connection (Latin America 40%)	Number of sewer connections is twice as high (see Table 17)	+ 43%
Eastern and Southern Europe does not have adequate WWT	Brought to North European standards	-8%
China has very little WWT	Number of plants is twice as high.	+ 33%
In China about 50% of WWT is anaerobic.	Ensured all WWT plants are aerobic. (Optimize WWT plant management)	-11%

Table 22 indicates that there is a large uncertainty associated with the estimates of the extent of WWT in developing countries. Also, significant uncertainties stem from the assumptions that estimate the degree of anaerobicity in WWT plants in developing countries and eastern Europe.

Uncertainties Associated With the N_2O Emission Estimates

N_2O is generated, as well as, absorbed during nitrification and denitrification and many uncertainties are associated with the development of reliable N_2O emission factors. Schön et al. (1993) summarizes the reasons for the uncertainties as follows:

- Emissions show strong variations over daily, as well as over longer, time frames. The reasons for these variations are not yet known;
- The influences caused by different WWT methods have not yet been quantified; and
- Development of a nitrogen mass balance to assist in quantifying emissions from specific sources in the WWT is very difficult.

The field tests detected N_2O emissions only from the anaerobic waste lagoons at the chicken processing plant; consequently, only one set of N_2O emissions data was obtained. No emissions were detected from the anaerobic waste lagoons at the two beef processing plants or the facultative lagoons at the two POTWs.

The field test emission factor, as well as, the emission factor developed from the literature must be used cautiously. The uncertainties associated with the activity data have been addressed earlier. The industrial activity data used in the U.S. estimate are believed to be relatively accurate. Also the activity value for conventional domestic WWT is believed to be fairly accurate, as it is based on population. The estimate for anaerobic domestic WWT includes an assumption on the degree in which COD decomposes under anaerobic circumstances. This assumption is based on expert judgement and may have large uncertainties associated with it.

TRENDS

Trends that affect CH_4 emissions from WWT are directly related to the amount of organics that degrade in wastewater under anaerobic conditions. Trends that affect N_2O emissions are related to anaerobic, as well as anoxic wastewater conditions associated with denitrification. On a global scale, only a small fraction of all wastewater is treated. Most wastewater is discharged into gutters or sewers where it may remain stagnant or through which it may flow into rivers or other surface water. Changes in the amount of wastewater that is treated are, of course inversely proportional to changes in the amount of wastewater that is not treated. Untreated wastewater may rapidly turn septic and may be a major source of GHG emissions. Therefore, trends in wastewater treatment as they affect GHG emissions, can best be discussed when adequate background knowledge on untreated wastewater, such as sanitation issues and open sewers, is included in the evaluation. As issues regarding untreated wastewater were not included in this study, this section on trends in WWT is necessarily generic.

Ongoing global industrialization, population growth, and also urbanization are likely to increase the annual industrial and domestic wastewater outflow. In many urbanized areas in developing countries, inadequate disposal of wastewater has become a major health issue. Although significant gains have been made in the provision of sanitation services, the influx of migrants into cities has nullified most efforts. In addition, the extended sewer line coverage has intensified the problems associated with the lack of WWT. As mentioned before, industrial and domestic wastewater is typically discharged raw into surface water, and rivers in developing countries are often little more than open sewers, making them unsuitable as a source for drinking or even irrigation water for down stream users. (Bartone 1990; Bartone 1994.) In some areas the inadequate disposal of pollutants has resulted in widespread ground water contamination, thus further reducing the availability of clean water (World Resources Institute, 1994).

The problems associated with the lack of WWT extend throughout the developing world including the countries of the former Soviet Union and most Eastern European countries. As far as domestic WWT, no significant improvements are expected for most of these countries in the near future (Draaijer, 1994). There are few exceptions such as the

former German Democratic Republic which has had access to West German financial and technical support. It should be noted that in some areas, problems associated with WWT and water availability have become so demanding that the implementation of improvements cannot be put off much longer. For example several arid countries, such as Tunisia, Turkey, and Bahrain are actively contemplating improved WWT with the main objective to recycle the effluent as crop irrigation water.

In regard to industrial WWT the situation may be a little better. Large industries are more easily regulated and monitored than indeterminate groups of urbanites. Also, such industries may be financed or managed by multinational companies that are more inclined to an integrated approach to WWT. Also, in some developing countries including countries such as Chile, Taiwan, Indonesia, and Singapore, notable economical growth has lead to a degree of prosperity making WWT affordable. Also, to sustain their high economical growth rates industries in these countries may be encouraged to implement source reduction and conservation programs which will impact wastewater generation. It is expected that these countries will increase efforts to clean their wastewater in the near future (Doppenberg, 1994).

Significant improvements in regard to WWT can currently only be expected from developed countries that have not had comprehensive WWT before. Examples of these countries are Belgium, Spain, Greece, and Turkey. Also, some east European countries, including Czechia, Slovenia, Hungary, and possibly Poland are experiencing significant economical growth that may enable them to finance improved WWT. Furthermore, the European Union in principal enforces uniform water and effluent quality regulations for its members, as well as its candidate members. For example, pressure to meet such regulations (in this case 90 percent reduction of load) has forced Spain to clean up its act. (WWEE, 1992.)

As mentioned before, preferred WWT throughout the world typically is aerobic (activated sludge) for large scale applications and facultative lagoons for small scale applications. Therefore, increased levels of WWT could lead to a reduction in GHG emissions. However, if WWT is favored over, for instance an ocean outfall, GHG emissions may increase. Without incorporating the contributions of untreated wastewater, it is not possible to properly estimate the effect of increased WWT on GHG emissions from this source category.

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APPENDIX A: SUMMARIES OF FIVE INTERVIEWS WITH WWT EXPERTS

In 1993, the state of knowledge, as reflected in the Report to Congress (EPA, 1994) was considered too limited to be a basis for improved emissions estimates. To obtain additional international WWT activity data, a data quest was undertaken in 1994 in Western Europe. Efforts focussed on the Netherlands, a German technical library and Belgium. The Netherlands is an international leader in environmental technology development, particularly in the fields of biotechnology and WWT. Data from a Belgian N_2O study have been included in the report and are not repeated here. Below are summaries of interviews with six Dutch wastewater experts.

INTERVIEW 1 (5/27/94)

Mr. Hans Draaijer, Advisor
GRONTMIJ
de Bilt, Netherlands

Grontmij is an environmental engineering firm and contractor (2,300 people). The majority of their activities are executed in the Netherlands. However, they also do work in Poland, Hungary, Russia, Japan, India, Taiwan, and China.

General

Draaijer expects that untreated wastewater is a significant global methane source since there is very little WWT worldwide. Draaijer suggests that statistics on the percentage of people with sewer hookup may be a useful activity indicator. In the Netherlands and West Germany, this number is 95 percent. In Belgium, it is less than 50 percent. Also, the fraction of wastewater that is treated per country might be very low. For instance, Belgium does not treat significant portions of their wastewater. Countries with tourism (e.g., Greece, Portugal, and Spain) usually are inclined to do a little more toward WWT, for public relations reasons. Outside of the OECD, the fraction of the wastewater treated is negligible.

India and Sri Lanka

Draaijer has spent extensive time in India. Grontmij works on two UASB projects in Mirzapur and Kanpur, India. The two UASB plants in India (on line April 94 and December 94) are funded with Dutch Government development aid. There is practically no sewerage in India. Usually sewage runs in a ditch to a river or lake. According to Draaijer, even a shallow ditch (30 cm) would quickly become anaerobic. This may be concluded from the black slime on top and the emanating bubbles. Anaerobic conditions are facilitated by high ambient temperatures. Also, wastewater in these ditches may have a very long residence time. The gradient might be very low and the gutter or canal may be filled with debris. The residence time would be an important parameter, according to Draaijer.

Draaijer points out that in municipal sewage, methanogens are already present in the liquid, as well as in deposits in pipe bends, etc. In sewer pipes, he expects the water to become anaerobic very rapidly, because the deposits will be a continuous source of methanogens. Eventually the sewage may make it to a larger body of water, typically a river. Draaijer thinks that rivers will become oxygen poor, but never totally anaerobic. He does not know

how much methane could be generated in semi-anaerobic rivers. (Note: rivers would have an aerobic facultative layer that breaks down any methane.)

In Sri Lanka, Draaijer also witnessed small channels into which sewage was discharged. They were almost completely clogged up and completely anaerobic.

Policy in India and Sri Lanka is to promote standardized aerated lagoons. Construction is simple, so proper operation will depend on maintenance (and energy cost for aeration). In Sri Lanka, Draaijer visited an industrial park with mainly large exporting or foreign owned companies. Such a cluster of wealthy companies would typically have WWT. In India, there are a few showcase WWT installations. In Varanasi, a brand new aerobic WWT plant was installed but it never ran, because of high energy cost. Draaijer said it had a large by-pass. Like many developing countries, India has modern regulations copied from a country such as the USA or Britain. However, there is no enforcement and some institutions or certain states may conduct a little monitoring.

What can be done in India (and similar countries) regarding the municipal sewage situation:

1. The awareness level of the population should be raised.
2. Build latrines or biogas vaults or tanks.
3. The retention time of the sewage in the ditches of pipes should be reduced. Build concrete ditches and make sure sludge deposits containing methanogen seeds cannot form.
4. Implement new technologies. UASB is interesting for developing countries. The technology is very simple. There are only two moving parts. The reactor can be built out of concrete blocks. It is recommended that the generated gas be burned in a direct user (such as a boiler), since electricity generation requires high technology expertise to operate, which is not always available.

Eastern Europe

In Eastern Europe, engineering development stopped 40 years ago. There are many antiquated WWT plants, most of which are not running. Almost all of the projects in Eastern Europe are being financed with West European funds. Firms like Grontmij are hired for studies and not to actually perform or assist with construction.

Case study from East Germany. A Dutch company bought a slaughter house in Nohra, near Weimar. Before, wastewater from the slaughter house simply drained into a forest. Grontmij was hired to build a new WWT plant. This plant was laid out with a capacity to treat all slaughter house waste (70 percent of capacity) and an additional 30 percent of sewage from a nearby town. Now the plant is finished but only the slaughter house waste is being treated. The sewers still have to be built (consider sewers part of infra-structure).

Within a very short period of time, East Germany will have to start applying West German regulations; therefore, a high level of activity may be expected in East Germany, funded for 100 percent by the Western part. All other Eastern European countries really have no money at all. Draaijer expects that the environmental situation in most countries is going to get worse before it gets better. Poland is a little less poor and may be somewhat of an exception. Draaijer does not know how many lagoons there are in Eastern Germany.

If a WWT plant would be built, it typically would consist of aerobic pretreatment (activated sludge reactor) which can remove 35 percent of the COD, and an anaerobic sludge digester. Sludge digesters may be a considerable methane source (Lexmond mentioned this also). In the Netherlands, methane leaks from the sludge digesters are estimated at 30 percent (?). In India, at sites inspected by Grontmij, 100 percent of the methane was emitted. In Eastern European countries, methane leakage from sludge digesters could well be 50 percent.

Methane Indicator

BOD is an aerobic test. Anaerobic organisms are more sensitive than aerobic. COD is better. Grontmij knows from experience what part of COD gets turned into methane: (1) Municipal wastewater: 80 percent of COD will turn into methane and 5 percent into sludge; (2) Industrial wastewater: low concentrations, 80 percent of COD will turn into methane and for high concentrations this number is 90-95 percent.

INTERVIEW 2 (5/31/94)

Mr. Doppenberg, Senior Advisor
Hoofdweg 490
IWACO
Rotterdam, The Netherlands

IWACO is an environmental engineering firm with 350 employees with a focus on water and wastewater technology.

General

According to Doppenberg, when dealing with developing countries, it is important to realize that people in developing countries have no influence. The system is rather feudal. People put up with bad circumstances, such as stench. They don't know any better.

In Africa, facultative lagoons have been in use since the late seventies, especially near smaller cities. In Asia, there would be few lagoons. The population density is too high. No quantifiable data are available.

Europe

In Eastern Europe, most cities have sewer lines; however, there is very little WWT. In rural areas septic tanks are being used. Money invested in WWT in Eastern Europe, it usually comes from the European Community and the European Bank for Reconstruction and Development based in London. Just like the World Bank, this bank might have information on the level of sanitation in Eastern European countries. If WWT systems are installed in Eastern Europe, they would typically be activated sludge systems with anaerobic sludge digestion. (Doppenberg mentions that sludge digestion installations are known to leak.) Doppenberg confirms that Belgium has no WWT. Wastewater flows straight into rivers. France is better.

Newly Industrialized Countries

Newly industrialized countries include countries such as Singapore, Korea, and Taiwan. Urbanization rates in these countries are between 4-6 percent per year. The result is that infrastructure cannot keep up with the urban growth. For instance, due to high freshwater demand, there may easily occur a water shortage in the region. This would not only reduce freshwater supply, but also reduce water flows in rivers. Yet the quantity of waste disposed of by water is on the rise. Taiwan is investing a lot of money in sewerage. Together with the World Bank, master plans have been developed.

Doppenberg expects that newly industrialized countries may start to purify in 10 to 20 years. He also believes that the wastewater problem caused by domestic sources is greater than that caused by industrial sources. Industrial sources can be pinned down and isolated more easily. Also, they have more financial resources. Environmental law enforcement usually has no teeth. Economic considerations prevail.

Indonesia

Indonesia has started an active program to get industry to clean up its wastewater. Doppenberg calls it: "a reasonably consequent approach." Currently, in Djakarta and also in the rest of Indonesia there is no sewerage and no WWT. Sewage is collected in gutters which discharge into larger canals. The water appears to be stagnant. From observation it may be judged to be completely anaerobic. When it rains the system is somewhat flushed out. Eventually it runs into a river or the ocean.

Recently, there was a study conducted at a laboratory in Delft which specializes in water engineering problems (contact Eelco van Beek or Jos Dijkman, 015-569353). The objective was to calculate the amount of water to flush the open sewers in Djakarta and to see if rain would provide this amount. The conclusion was negative. Rainwater cannot provide enough flow for the open sewers to do the job. Relief can only come from reduction at the source (sanitation programs). Issues relating to developing the mass balance include, the amount of sewage that seeps away through the soil, the water evaporation rates, and "fast run off" losses.

Mr. Doppenberg related his experience from a boat ride off the Djakarta coast towards an archipelago called the Thousand Islands. The speed boat ride was about an hour. Coming back, half an hour off shore, there is an obvious and sudden change in the water quality. Clean seawater changes into brown/black water, which apparently is not aerobic.

Methodology proposed by Doppenberg

In order to develop CH_4 emission estimates from domestic wastewater in developing countries, Doppenberg's suggests to eliminate the rural population contributions, collect sanitation data from the World Bank and the European Bank for Reconstruction and Development, calculate how much methane can be formed in open sewers.

For industrial wastewater he suggests to eliminate cooling water contributions, see which part of industry is located on rivers and assess if wastewater from these sources can be excluded as a methane source, assess if the conditions and retention time are sufficient for industrial

wastewater to turn anaerobic before it reaches the river, develop emission factors for these situations, estimate emissions from WWT.

Innovative Methodologies

Suitable Technologies (for newly industrialized countries and Developing Countries). Population density or urbanization determines the type of WWT that is most suitable.

- Large scale would be aerobic. Large city, high density: sewerage and treatment plant. (If something breaks down in aerobic WWT, it will be the aerator, since that is the mechanical part.)
- Medium size might actually be lagoons. Smaller cities, less urban: introduce sewerage in phases, build WWT plant which can be expanded easily.
- Small scale projects: anaerobic WWT is suitable. Even smaller, just a neighborhood: UASB. Eventually you can switch to centralized WWT.
- Individual housing, low population density: septic tanks and basic latrines.

An issue with anaerobic WWT is that there is typically no natural gas piping network, so the gas cannot be sold or transported by existing pipeline. An option would be to store the biomethane in bottles. Doppenberg points out that it is all a matter of economics. If other types of energy are cheap, you can forget selling the digester methane. For instance, Indonesia has a lot of oil. A market is slowly being created for natural gas. If natural gas is available, nobody will want the digester gas. On the other hand, wood is getting scarce in many countries.

INTERVIEW 3 (6/1/94)

Mr. W.M. Wiegant and Ms. A.T.J.J. Kalker,
HASKONING, Royal Dutch Consulting Engineers
Nijmegen
The Netherlands

Haskoning is a large international civil and environmental consulting/engineering firm with wastewater related projects in many countries, including India, Japan, South America, and Africa. Recently Haskoning was commissioned a project to assess needs to clean up the Danube river. As part of this project they will produce estimates of wastewater discharges into the river.

General

Wiegant believes that on a global scale domestic sewage is a larger methane source than industrial wastewater. Significant industrial sources are the food processing and agricultural industries; a large plant may produce wastewater quantities equivalent to that of a city of a million inhabitants. Industrial WWT, if any, would typically be a lagoon. Exceptions are plants that have been built by the British. For some reason they favor trickling filters. Either method requires sludge treatment. Wiegant stressed the importance of sludge formation. In a sewer, half of the dry solids may become sludge. Only the remaining half

then would be the potential methane source. Wiegant says that for domestic sewage, dry solids is a good parameter for estimating methane potential.

Wiegant believes there are many lagoons in South America.

According to Wiegant, rivers or lakes may indeed become facultative with excessive BOD inflow. Wiegant does not know how to assess the fraction of methane that still might be emitted from facultative rivers. Wiegant confirms that seas or oceans can indeed turn anaerobic. However they will not emit methane. The reason is that there are sulfates in the sea water. "H_2S-ogens" are dominant compared to methanogens.

South America, Colombia

Ms. Kalker spent several years in Colombia in the late eighties. At that time, there was practically no WWT in the country. There are WWT laws, but there is no enforcement. Only recently the Government Department of the Environment was established. If Kalker had to give a number, she would say that currently (1988?) no more than 2 percent of wastewater is treated in Colombia.

In South America the alcohol industry is a large polluter. The production of one liter of alcohol produces five kg of COD. The palm oil industry seems to be somewhat of an exception, and has historically received more than average attention, possibly because the palm oil process is highly polluting. Kalker believes they are using lagoons.

The city of Cali, Colombia, population 2,000,000, has recently developed a master plan to treat its wastewater. There was already a sewage system in place. (Note: there is anecdotal evidence that other South American countries, such as Brazil, also have extended sewer systems). In the early 1990's, a UASB WWT plant became operational. This plant takes care of sewage from 200,000 people or 10 percent of the population of Cali.

India

The fraction of wastewater treated in India is negligible. Typical WWT (if existent) would be aerobic (activated sludge reactor). Nevertheless, Wiegant would recommend anaerobic WWT for warm countries. Experience has been positive. It requires practically no energy or maintenance. You can avoid pumping by using natural gradients. Then the only remaining piece of mechanical equipment is the rake mechanism at the top. The methane is usually flared off.

Composting

At a WWT plant, the remaining solids left after sludge digestion may be composted. A compost heap is anaerobic (according to Wiegant). The inside is anaerobic, but the outside layer is aerobic and will break down the methane again. Even if the compost is turned over, the fresh oxygen is depleted rapidly and anaerobic conditions will be recreated within the hour.

INTERVIEW 4 (5/24/94)

Mr. Karel Jansen,
Wastewater Expert Netherlands
Heineken Breweries, Zoeterwoude, The Netherlands.

In 1993, Heineken produced 1,480 million gallons of beer with operations in 50 countries. For every gallon of beer, 5 to 9 liters of wastewater are generated. Typically, wastewater from a brewery has BOD = 1,400 and COD = 2,400 (rule of thumb: COD = 1.8 x BOD). The wastewater also contains significant amounts of nitrogen. Wastewater from one hundred liters of beer will require 540 grams of O_2. In aerated lagoons 35 percent of the COD and 50 percent of the BOD can be removed daily.

Worldwide Heineken policy is to treat wastewater in aerated lagoons. Mr. Jansen pointed out that aeration requires energy and therefore, costs money. As such, there may be an inclination to under-aerate.

Heineken is constructing new anaerobic WWT systems at breweries in the Netherlands and in Spain, and in the future, possibly in other European countries. These plants are UASB reactors and are meant for pretreatment and can remove 80 to 90 percent of all pollutants. The main reason for switching to anaerobic treatment would be space constraints. Also, Heineken actively uses the biogas as fuel in on-site boilers or, for instance in space heating or electricity generation for offices.

INTERVIEW 5 (5/24/94)

Ms. Dr. Ir. G. Zeeman
Department of Environmental Technology
Wageningen Agricultural University
Wageningen, Netherlands

Anaerobic treatment is of particular interest to Wageningen Agricultural University and ongoing research is conducted to study and improve anaerobic WWT systems, in particular the upflow anaerobic sludge blanket digester (UASB), which was invented here. The UASB is a mechanically simple pretreatment technique that requires little space and maintenance. It is suitable for small to medium size wastewater flows and has been employed for treatment of sewage, as well as, wastewater from the following processes: alcohol, sugar, most food and beverages, fermentation, and petrochemicals. The key to the process is the formation and maintenance of a suspended granular anaerobic sludge which allows high upflow wastewater velocities and as a consequence high COD loading rates (up to 20 kg COD/m^3.d). Gas, water and return sludge are separated in the top of the vessel by a system of fixed baffles. Disadvantage of the system is that methanogens are very sensitive to changing environmental conditions, such as pH, temperature, presence of toxins and/or nutrients. (Information from Biothane International, phone 011.31.15.700111. and Paques, phone 011.31.5140.8500.)

Dr. Zeeman and Ms. Lexmond (not present) have worked on a global inventory of waste and wastewater flows for specific industries that emit methane and thus may be suitable for anaerobic WWT (Lexmond and Zeeman, 1994; Lexmond and Zeeman, 1995). Activity data

were collected in part by interviewing environmental professionals from developing countries. These people were in the Netherlands for training. The 1994 and 1995 reports of Lexmond and zeeman are quoted extensively throughout this report and are not discussed here again.

Also, Zeeman and Lexmond hope to get funding for a new project. The aim of this project is to categorize global non-CO_2 greenhouse gas control technologies. Information will be provided with respect to: state-of-the-art technologies, emission reduction potentials, costs of controls, prospects for further development and (nontechnological) constraints, all per type of wastewater. The lead contractor will be Ecofys in Utrecht, the Netherlands (drs. de Jager, phone 011.31.30.732144).

Zeeman disapproves of using BOD as a parameter for methane emissions because BOD determination is an aerobic test. The relationship between BOD and produced methane will depend on the type of wastewater. To compensate for this effect Lexmond introduced a factor which is specific for different types of wastewater.

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APPENDIX B: WASTEWATER TREATMENT METHODS

Removal of contaminants from wastewater is done by physical, chemical, or biological means or a combination thereof. Simple treatment methods in which the application of physical forces predominates are screening, mixing, and sedimentation. Filtration, flocculation, and flotation are more complicated physical treatment methods. Precipitation, adsorption, and disinfection are examples of common chemical treatment methods. Biological treatment is used to remove the biodegradable organic substances from the wastewater. Basically, these substances are converted into gases (including GHGs) that can escape to the atmosphere and into biological cell tissue that can be removed by settling (sludge). Biological treatment is also used to remove nutrients (such as dissolved nitrogen and phosphorus compounds) from the wastewater. (Metcalf & Eddy, Inc., 1991.)

Another common classification of WWT methods is in primary treatment (or pretreatment), secondary treatment, and tertiary (or advanced) treatment. In primary treatment, physical operations are used to remove floating and settleable solids from the wastewater. In secondary treatment biological and, to a lesser extent, chemical processes are used to remove most of the organic matter. Subsequently, in tertiary treatment combinations of processes are used to remove the remaining constituents and pathogens in order to upgrade the quality of the treated wastewater. Tertiary treatment processes include: maturation/polishing ponds, filtration, carbon adsorption, ion exchange, disinfection, and phosphorus and nitrogen removal (nitrification/denitrification). Denitrification may be a source of N_2O. Otherwise, tertiary treatment processes are not considered to have potential for GHG emissions.

The text below gives an overview of the processes that are typically found in a standard municipal WWT plant or POTW treating domestic sewage and possibly some industrial wastewater. Particular industries that (pre)treat their liquid waste may employ different treatment processes, which are not included in the text below. Standard municipal WWT plant systems are only economical if they have a certain minimum size. Small community WWT systems may include processes that are principally similar to that of large municipal WWT plants, or they may use processes that are entirely different, such as land treatment. Also, domestic wastewater may be treated in septic tanks or pit latrines. The description of small scale systems is not included in this report. Future research will be aimed at estimating GHG emissions from such systems and from untreated wastewater.

Primary Treatment

Upon entering a municipal WWT plant, wastewater will typically first encounter a coarse screen to remove large size solids, such as rags and wood. At this location, the velocity of the wastewater will be relatively high to prevent settling of solids and the screen itself will cause additional turbulence in the wastewater. This turbulence is conducive to stripping a significant fraction of the gases that may have been dissolved in the wastewater. Such gases may include VOCs from industrial facilities or biodegradation products, such as CO_2, CH_4, or H_2S that were generated in closed sewers.

The ensuing primary treatment step typically incorporates a reduction of the wastewater velocity to bring about settling of TSS (sedimentation). Settling tanks for coarse particulates are often called "grit chambers," whereas finer solids are separated from the wastewater in a "clarifier." (Clarifiers may also be included as intermittent steps in secondary treatment.) Other primary WWT may consist of oil and grease removal by skimming the surface of, for instance the clarifier.

Secondary Treatment

Secondary treatment is a combination of biological processes in which organic matter is biodegraded in an aerobic environment, sometimes in combination with an anaerobic phase. The oxidized TSS fraction will settle as sludge. Secondary biological treatment processes may be divided into:

- Stabilization lagoons (also referred to as aerated/aerobic lagoons, oxidation ponds, anaerobic lagoons, facultative lagoons);
- Trickling filters; and
- Activated sludge processes.

Stabilization Lagoons—

Treatment in stabilization lagoons is the most natural, effective and economically viable process, especially in regions with plenty of sunshine and available land. Depending on the secondary treatment process, the removal efficiency may be between 75 to 95 percent of BOD and 80 to 95 percent of TSS. To obtain optimal results, several lagoons may be employed in series (e.g., an anaerobic primary pond followed by one or more facultative or aerobic lagoons, followed by oxidation ponds). (Oxidation ponds are also called maturation or polishing ponds and are considered tertiary treatment.)

Facultative lagoons are those in which the upper layer is maintained as an aerobic zone and the lower one as an anaerobic zone. The upper layer can retain an aerobic status, due to algal photosynthesis, as well as weather influences, such as wind and rain. The depth of facultative lagoons ranges from 1 to 2.5 m depending on the temperature and the type of wastewater to be treated. These lagoons are normally used as primary or secondary units to anaerobic or aerated lagoons for industrial wastewater.

In oxidation ponds aerobic conditions are also maintained by the natural photosynthetic process by algae and by surface aeration. Unaerated lagoons are usually very shallow (e.g., 0.6 m), whereas the depth in aerated lagoons may be around 1.5 meters, reducing the area requirements for lagoon construction significantly. Aerobic lagoons are typically used for treating domestic sewage that has had some form of pretreatment.

Anaerobic lagoons can be compared to a digester and are routinely used for the treatment of very strong wastewater, such as from slaughterhouses. Their primary function is to reduce the initial high demand of oxygen which otherwise would be required for oxidation of the organics. The effluent from anaerobic lagoons requires additional aerobic treatment to meet most quality standards. The anaerobic degradation process of organic matter involves two types of bacteria. Facultative organisms break down large

organic molecules into smaller molecules, such as organic acids, while other bacteria transform the organic acids into CH_4 and CO_2. Simultaneously, other bacteria convert organic nitrogen into NH_3 and H_2S may also be formed.

Design criteria for different types of lagoons are summarized in Table B-1. Anaerobic lagoons may have depths that exceed 5 m. The effect of retention time on BOD removal in anaerobic lagoons is relatively minor. The storage of deposited solids seems to be of primary importance and the actual liquid retention time should be such that the CH_4 producing bacteria are not washed out of the system. The optimum retention time is 5 days (Mullick, 1987). Anaerobic lagoons operated with higher hydraulic retention times (HRTs) have been found to be facultative rather than anaerobic. Unlike for aerobic and facultative lagoons, design criteria for anaerobic lagoons are not based on area considerations, as the processes in the pond do not depend on insolation. Recommended loading rates vary between 0.1 to 0.4 kg BOD/m^3/day, depending on the type of waste and water temperature. BOD removal efficiencies may be around 65 to 80 percent. (Mullick, 1987.)

TABLE B-1. DESIGN CRITERIA FOR LAGOONS

	Aerobic	*Facultative*	*Aerated*	*Anaerobic*
Organic loading	*85-170 kg BOD /ha/day*	*17-55 kg BOD /ha/day*	*25-400 kg BOD /ha/day*	*0.1-0.4 kg BOD/m^3/day*
Depth (m)	0.6	0.9-2.5	1-3	2-5
Retention time (days)	5-20	10-100	3-20	2-30
pH range	6.5-10.5	6.5-9	6.5-8	6.8-7.2
Temp. Range (•C)	0-40	0-40	0-40	7-40
Temp. Optimum (•C)	20	20	20	30-35
BOD (%)	80-95	75-95	80-95	50-80

Based on Mullick (1987) and Metcalf & Eddy (1991).

Trickling Filters—

Trickling filters are large circular tanks filled with porous elements, such as crushed rock, slag, or molded plastic. The wastewater is mixed with air by spraying it onto the elements after which it trickles down to the bottom of the tank to be removed or recirculated. The microorganisms that are responsible for breaking down the dissolved and suspended organics live in a slimy layer on the surface of the elements. Trickling filters are considered to be entirely aerobic and will, therefore, be a source of CO_2 emissions to the air. Also, due to the agitation of the wastewater during the spraying action, gases that are dissolved in the wastewater will easily be stripped. A high rate trickling filter may have a loading rate of 0.75 kg BOD/m^3/day. The BOD removal efficiency is approximately 80 percent.

Activated Sludge Process—

The activated sludge process is a continuous-flow aerobic biological process for the treatment of domestic and biodegradable industrial wastewater. The process provides a high-quality effluent and is characterized by the thorough mixing of microorganisms, oxygen, and wastewater induced by the aeration system. The mixture is referred to as "mixed liquor." During the aeration phase bacteria convert organic matter into cell matter, energy, CO_2, NH_3, water (H_2O), and other end products. The mixed liquor is usually recirculated. Excess sludge is removed from the process and effluent from the aeration basins will typically be discharged into a clarifier where the microorganisms settle out and are recycled to the aeration basin.

There are many varieties to the activated sludge process, some of which comprise two or more separate aeration steps. Therefore, it is difficult to produce overall characteristic data; however, the following design data from Standard Handbook of Environmental Engineering (1990), applicable to a "conventional" activated sludge system, may provide an indication:

- volumetric loading 0.4-0.8 kg BOD/day/m^3;
- detention time 4-8 hrs;
- mixed liquor recycle 50-100 percent;
- sludge retention time 5-10 days;
- sludge production 0.5 kg/kg BOD.

Nitrification and Denitrification

Nitrification and denitrification are an integral part of WWT. Nitrification is the oxidation of NH_3 to nitrate and water and takes place in aerobic reactors such as trickling filters or rotating biological contactors, either separately or in combination with carbonaceous matter removal. Denitrification is the reduction of nitrate and nitrite to N_2O and nitrogen (N_2). It may be classified as advanced treatment and takes place under absence of oxygen. The presence of dissolved oxygen will inhibit the process. Also, the denitrification organisms are sensitive to changes in temperature and pH. Usually an extra carbon source (i.e., methanol) is required for cell growth. Separate stage denitrification may take place in plug-flow type reactors or in column reactors. To avoid the cost of carbon addition, processes have been developed that combine nitrification/ denitrification processes with other treatment steps. These combined systems are characterized by an aerobic and an anoxic zone and recirculation of part of a stream that is rich in organic carbon (Metcalf & Eddy, 1991). N_2O emission models are discussed separately in the section entitled "Additional Information on Greenhouse Gas Emissions from WWT."

Sludge Treatment and Disposal

Sludge withdrawn from various stages of a WWT plant normally needs to be treated further to ensure its safe and most cost-effective disposal. Economic considerations play an important role, because the cost of sludge treatment and disposal may represent up to half the cost of the preceding liquid treatment facilities. Aerobic bacteria produce considerably more sludge than anaerobic bacteria, given similar loadings and efficiencies.

The volume of sludge produced usually ranges from 0.3 to 0.7 percent of the volume of wastewater treated and depends on the BOD or TSS loading. In conventional plants (primary treatment followed by activated sludge treatment) approximately 0.6 to 1.0 kg sludge (dry solids) are produced per kg BOD. Sometimes a value of 0.025 to 0.03 kg (dry solids)/person/day is used. For pond systems a rate of sludge accumulation of 0.03 to 0.08 m^3/person/yr is used. This implies that pond sludge removal would be necessary every 2 to 5 years (Mullick, 1987). Sludge generation in lagoons will vary widely. In cold climates sludge will accumulate faster than in warm climates due to sedimentation of unbiodegraded matter. Fresh sludge typically has a moisture content of up to 99 percent and is difficult to consolidate. Methods for sludge treatment are:

- Aerobic and anaerobic digestion (also referred to as stabilization);
- Conditioning (e.g., use of flocculants);
- Concentration and dewatering (e.g., centrifugation or filter press);
- Composting; and
- Drying.

These sludge treatment processes are often used in combination with each other. Aerobic and anaerobic digestion are the only sludge treatment processes that involve significant breakdown of the sludge to produce CO_2 and/or CH_4 and other end products. Therefore, they will be discussed in some detail below.

Aerobic Digestion—

Stabilization of sludge by aerobic digestion is usually employed for secondary activated sludges. The operating costs are relatively high, because the aeration necessary for proper mixing of the sludge is energy intensive. On the other hand, capital costs are lower and operation and maintenance is easier compared to anaerobic digestion. Because of the energy requirements aerobic digestion is best suited for smaller treatment facilities. Performance is strongly affected by temperature and below 10°C sludge stabilization may be insufficient (Mullick, 1987; Standard Handbook of Environmental Engineering, 1990.) The reduction of volatile solids is about 30-50 percent, depending on the temperature and sludge retention time may vary between 12 to 30 days.

Anaerobic Digestion—

Anaerobic digestion of sewage sludge results in conversion of readily degradable organic matter into CH_4 (60 to 70 vol. percent), CO_2 (20-30 vol. percent), H_2S, other gases, and water, leaving a biologically stable residue. Volatile solids are reduced by 40 to 60 percent. In addition a significant reduction in pathogenic bacteria occurs. Anaerobic digestion takes place in cylindrical tanks with a conical bottom. The tank cover is usually floating and auxiliary equipment is required for gas collection, mixing and heating.

Digester gas, which has a heating value of around 600 British thermal units (Btu)/ft^3 can be a valuable resource. Even though the gas produced by anaerobic digesters is meant to be collected, digesters should be considered as potential GHG sources, because significant amounts of gas may leak to the air (Lexmond and Zeeman, 1994).

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APPENDIX C: EFFECT OF WATER AND AMBIENT AIR TEMPERATURE ON CH_4 EMISSIONS AND COD REMOVAL RATES IN ANAEROBIC LAGOONS

The temperature of wastewater in an anaerobic lagoon is expected to have a significant effect on the decomposition of organics in wastewater and on biogas generation. Lettinga et al. (1983) studied domestic sewage treatment in a 120 l pilot upflow anaerobic sludge blanket (UASB) reactor and collected numerous influent and effluent data over a period of almost a year. COD removal efficiency and biogas production data from this study are plotted against temperature in Figure C-1.

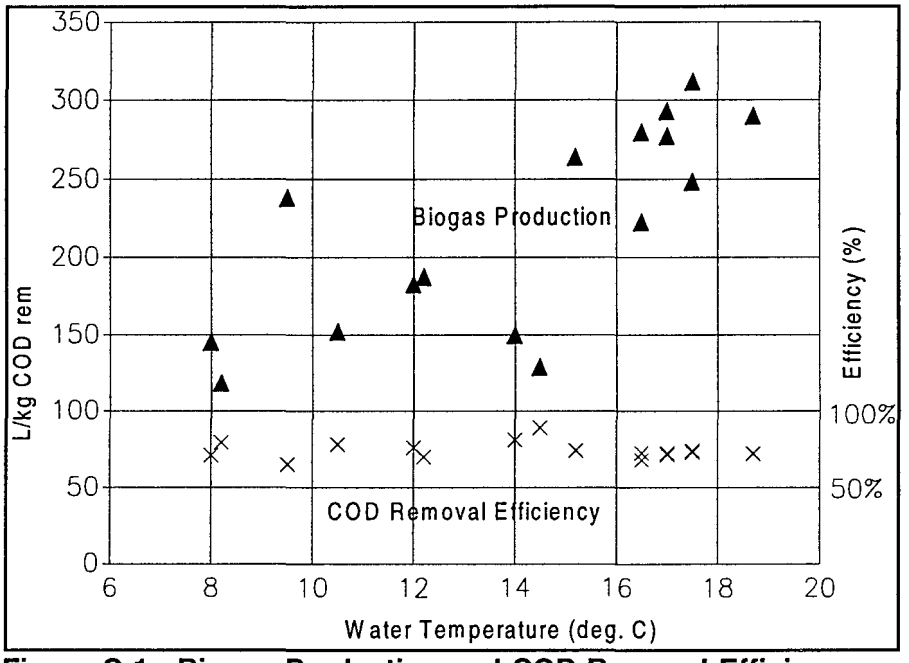

Figure C-1. Biogas Production and COD Removal Efficiency as a Function of Temperature in a Pilot UASB Reactor Treating Domestic Sewage.

According to Figure C-1 the COD removal efficiency does not vary significantly with temperature. The biogas production, however, decreases significantly and drops to about one third of the 20°C value. Lettinga does not provide data on the composition of the biogas, but as the reactor is anaerobic, it may be assumed that the gas is predominantly CH_4. A comparable study was conducted by Viraraghavan and Kikkeri (1990) who monitored the effect of temperature on anaerobic filter treatment of dairy wastewater for various retention times at three set temperatures: 12.5, 21, and 30°C. For a 6-day retention time, they observed a slight drop (about 10 percent) in COD removal efficiency from 82 percent to 74 percent over the 30 to 12.5°C temperature range. The CH_4 production rate however, dropped from 0.29 to 0.08 m^3/kg COD (72 percent) for that temperature range (Figure C-2).

The COD removal efficiency curves in Figure C-2 indicate a non-linear relationship with temperature. Toprak (1993) also summarizes findings that manifest a non-linear curve for CH_4 emission rates versus lagoon temperatures. From Figure C-2, it is unclear if the accelerated drop in CH_4 generation occurs at 21°C or at lower temperatures (because the lines consist of only three points). But according to Draaijer (1994) the 20 to 21°C zone is significant. Draaijer relates the following experience concerning a full scale UASB system in India: "The treatment efficiency remained constant irrespective of the decrease in temperature during winter time; even though there was a clear decline in gas production during about four weeks in January, when the sewage temperature decreased to 20°C, the biogas production increased rapidly again when the sewage temperature went up." All studies cannot be quantitatively compared, because each uses different output data. Nevertheless, it may be concluded in general that CH_4 emission rates in an anaerobic wastewater treatment system begin to drop at about 21°C and that below about 12 to 15°C CH_4 emissions are insignificant.

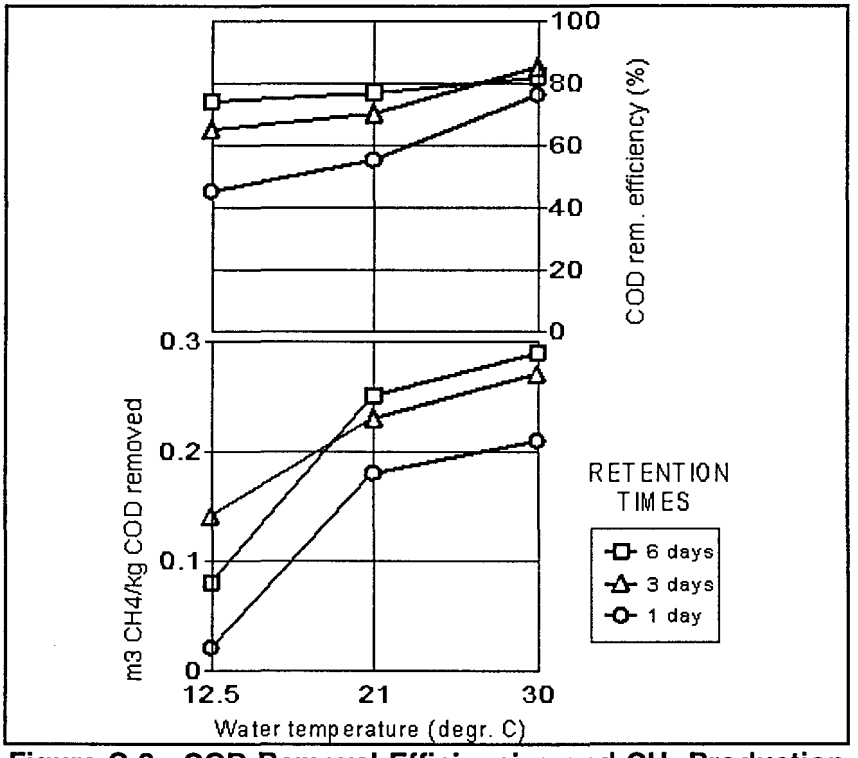

Figure C-2. COD Removal Efficiencies and CH_4 Production as a Function of Temperature

As mentioned earlier, Lettinga's data in Figure C-1 show no apparent drop in COD removal with falling temperatures, whereas Viraraghavan and Kikkeri (Figure C-2) found only a slight decline. Both studies describe systems (an UASB reactor and anaerobic filter) that are believed to be more efficient than ordinary anaerobic lagoons and, hence, COD removal efficiencies for lagoons may be lower. Also, removal efficiencies for lagoons will depend on many other factors, including retention time (see Figure C-2), type of

wastewater, and the lagoon layout. Merker (1996) gave the following generic numbers for anaerobic U.S. poultry processing waste lagoons: BOD removal efficiency in summer is about 70 percent and in winter about 40 percent.[14] In spite of lower removal efficiencies in winter, it is apparent that in an anaerobic lagoon in a country such as the United States, significant amounts of undegraded COD stay behind in winter. When in spring the water temperature increases again to around 15°C partial anaerobic degradation of this stored COD may again start up, whereas, at 21°C optimum degradation temperatures will again have been reached. Accordingly, in late spring and summer, CH_4 emissions may be expected to be significantly higher than predicted using theoretical estimates, whereas, in winter they may be expected to be near zero. It is unclear if degradation and thus, gas emissions peak as soon as the 21°C mark is reached, or if there is a certain lag time.

Lagoon water temperatures may be related to average ambient air temperatures. Metcalf and Eddy (1991, p. 606) include an equation (Equation 7) for a completely mixed lagoon and state that the complete mixing assumption is acceptable as long as the depth of the lagoon does not exceed 12 ft (3.7 m).

$$T_w = \frac{AfT_a + QT_i}{Af + Q} \qquad (14)$$

where:
- T_w = lagoon water temperature (°C);
- T_a = ambient air temperature (°C);
- T_i = influent water temperature (°C);
- A = lagoon surface area (m^2);
- Q = flow rate (m^3/day); and
- f = proportionality factor of 0.5.

The factor f incorporates the appropriate heat transfer coefficients and includes the effect of surface area change due to aeration, wind, and humidity. For the Southeastern United States $f = 0.5$. No values for f for other areas are given so this number was also used for the Southern United States. Anaerobic lagoons usually have fairly standard areas and depths, governed by the flow and required retention time. Hence, representative values for Q and A can be obtained fairly easily from actual data or from design criteria. T_i, however, is difficult to determine by methods other than direct measurement. Before it reaches the lagoon, wastewater may travel a considerable distance through an underground sewer line, or it may travel through an above ground pipeline, as is often the case with industrial wastewater. In addition, it may pass through weirs, screens or settling tanks, where it is subject to short- and long-term climatic influences, such as solar radiation, wind, humidity, and ambient air temperature (T_a) variations. Here, it is assumed that T_i is equal to T_a, which, in turn, implies that T_w is

[14] The removal rate for the poultry plant in the field test report is considerably higher (92 percent). The retention time at the field test plant was 16 days.

equal to T_a. As long as T_a is an average value, not reflecting short term swings, this approach appears reasonable.

Figure C-3, shows approximations of monthly water temperatures for two lagoons in Texas. One curve is for a hypothetical lagoon in Amarillo, Texas, and was developed using Equation 7 and the assumption discussed above. Ambient air temperatures came from The National Atlas (Department of the Interior, 1970). The second curve represents actual effluent water temperatures for a facultative municipal wastewater lagoon in the Southwestern United States, provided by the plant operator during the field tests (Eklund, 1996). Effluent temperatures are used here as a surrogate for actual water temperatures. Figure C-3 is divided into three temperature zones which reflect intensity of anaerobic degradation (and thus, CH_4 emissions). The approximate duration of each zone in months may be determined from Figure C-2 and is included below.

Zone:	Optimum Degradation	Partial Degradation	Zero Degradation
Facultative lagoon	4½ months	3½ - 5 months	2½ - 4 months
Hypothetical lagoon	3½ months	2 - 5 months	5½ - 6½ months

Based on the information above it may be concluded that in the Southern United States optimum temperatures for organics (COD) degradation exist only for a relatively short time of the year (i.e., 3½ to 4½ months). During 2½ to 6½ months, no degradation of organics takes place and during the remainder of the year only partial degradation is likely to occur. During the Partial and Zero Degradation phases, undegraded COD logically must accumulate in the lagoon. As Draaijer indicated, when the water temperature rises above 21°C during the 3½ to 4½ months, Optimum Degradation period (summer), this COD will yet be degraded. During this period, fresh COD will also be degraded and consequently, CH_4 emissions are likely to be significantly higher compared to emissions from an identical lagoon in a climate with a temperature that is constantly above the 21°C mark. Without further tests it is unclear if CH_4 generation from "old" COD happens evenly or peak-wise. For example, there may be a peak in microbial activity shortly after the Optimum Degradation phase is reached, and CH_4 emissions during this peak time may be many times higher than what would be expected as a yearly average. If CH_4 generation from "old" COD is more gradual, it may be expected that overall summer emissions are at least twice as high as what would be expected at an ideal lagoon.

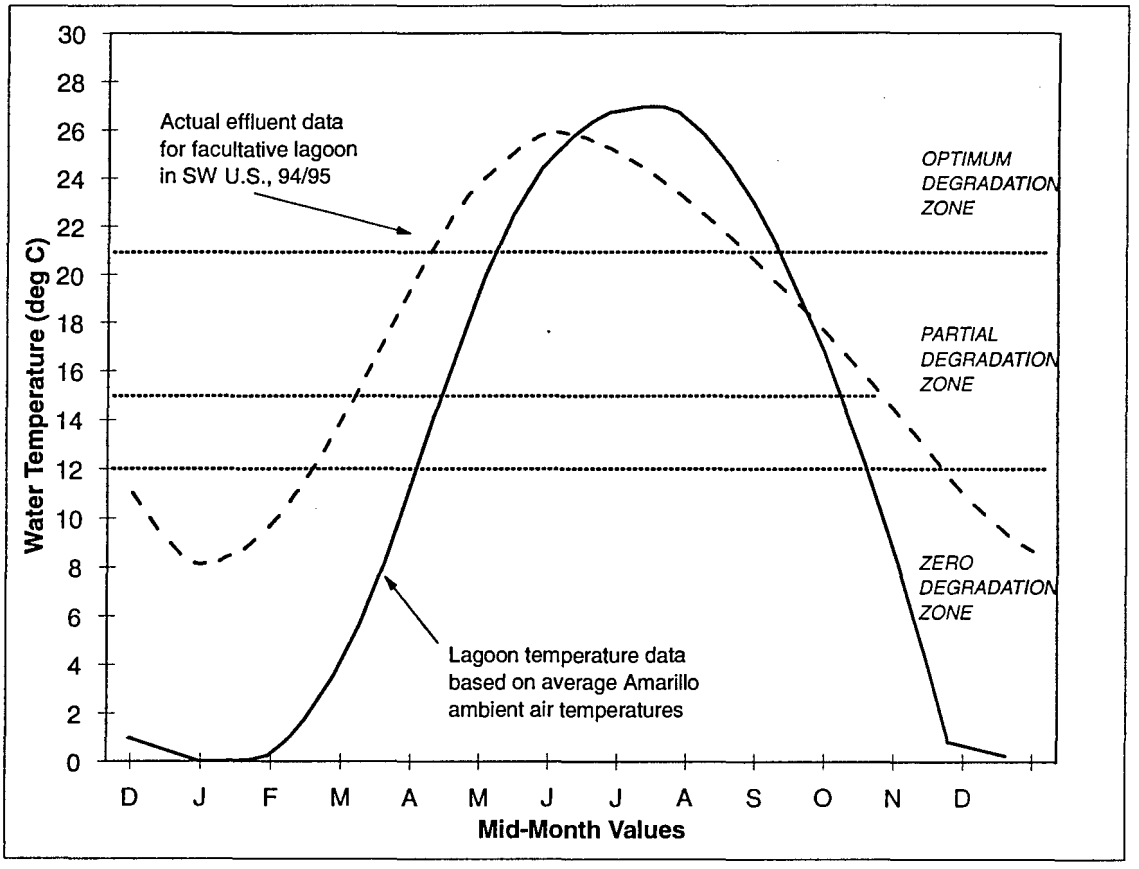

Figure C-3. Monthly Water Temperatures for Two Lagoons in the Southern United States

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