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THESIS

NITROUS OXIDE EMISSION SAMPING METHOD FOR WASTEWATER TREATMENT PLANT WITH BIOLOGICAL NITROGEN REMOVAL

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A Thesis Submitted in Partial Fulfillment of
the Requirements for the Degree of
Master of Engineering (Environmental Engineering)
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According to general method of nitrous oxide (N_2O) emission measurement for wastewater treatment plant (WWTP) with biological nitrogen removal (BNR) should follow U4R07 protocol: Characterization of Nitrogen Greenhouse Gas Emission from Wastewater Treatment BNR Operation. The protocol suggests using the chamber properly match with the isolating flux chamber to collect N_2O gas from WWTP. The commercial chamber could be ordered from http://www.fivesenses.com. However, this chamber is significantly expensive and has to import from abroad. For this reasons, the onsite emission gas collecting chamber (OSEGCC) for N_2O emission sampling method was developed. The results from this research revealed that there is truly nitrous oxide emission from full scale WWTP Thailand by delivery grab samples.

The OSEGCC was tested for leakage before it was used to collect sample in the field of WWTP with BNR. The leakage test of the OSEGCC was conducted by observation white smoke from aroma joss sticks for a half an hour.

To collect N_2O gas in the field, the OSEGCC was floated in an anoxic zone of BNR of activated sludge with BNR for 24 hours. The OSEGCC was tied by three concretes boxes to protect turn over in 7 meter deep BNR. The bottom rim of the OSEGCC would be with BNR about 4 inch or 7L. The headspace of the OSEGCC would be high 8 inch or 14L at atmospheric pressure. The amount of grab sample was collected to the 10 L tedlar bag. The samples were taken to analyze N_2O concentration at the Environmental Research and Training Center (ERTC), Thailand.

The N_2O concentration from WWTP with BNR in anoxic and aerobic zones was 25 ppm or 0.44% N_2O emission of the nitrogen load and 17 ppm or 0.35% N_2O emission of the nitrogen load, respectively. The N_2O result production from WWTP with BNR from this work could be used as a guideline for study N_2O production in the future.

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Student's signature Thesis Advisor's signature

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Finally, my most appreciation devotes to my pass away parents, who teach me to be the patient, devoted person.

Suntaya Mingmongkol

March 2012

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LIST OF ABBREVIATIONS

AS	=	Activated Sludge
BNR	=	Biological Nitrogen Removal
COD	=	Chemical Oxygen Demand
COD/N	=	Chemical Oxygen Demand and Nitrogen Ratio
CO_2	=	Carbon Dioxide Gas
CM	=	Centimeter
CFCs	=	Chlorofluorocarbon
$C_5H_7O_2N$	=	New Cell
Dia.	=	Diameter
DO	=	Dissolved Oxygen
ERTC	=	The environmental research technology centre Thailand
Ft.	=	Foot
GHG	=	Green House Gas
H_2	=	Hydrogen gas
H_2O	=	Water
HCO_3^-	=	Bi Carbonate
M	=	Meter
NH_3^+	=	Ammonia Nitrogen
NH_4	=	Ammonium gas
N_2	=	Nitrogen gas
N_2O	=	Nitrous Oxide gas
NO	=	Nitric Oxide gas
NO_2^-	=	Nitrite
NO_3^-	=	Nitrate
OSEGCC	=	Onsite Emission Gas Collecting Chamber
SEFIC	=	Surface Emission Flux Isolating Chamber
PPM	=	Part Per Million
PPB	=	Part Per Billion
Mg/L	=	Milligram per Liter
M	=	Meter
TKN	=	Total Kjeldahl Nitrogen
IPCC	=	The Intergovernmental Panel on Climate Change
PCFs	=	Per fluorocarbon
U4R07	=	Protocol of Characterization of Nitrogen Greenhouse Gas Emission from Wastewater Treatment BNR Operations
USEPA	=	US Environmental Protection Agenda
WWTP	=	Wastewater Treatment Plant
WERF	=	Water Environmental Research Foundation

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NITROUS OXIDE EMISSION SAMPLING METHOD FOR WASTEWATER TREATMENT PLANT WITH BIOLOGICAL NITROGEN REMOVAL

INTRODUCTION

There are six green house gases (GHGs) such as carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), surfer hexafluoride (SF_6), Chlorofluorocarbon (CFCs) and Per fluorocarbon (PFCs). N_2O is laughing gas and anesthetic gas which uses in dental treatment, surgery in the hospital and popular use in the mobile acceleration. The USEPA reports that 69% N_2O mostly emits in from agricultural soil management and 1.5 % is from wastewater treatment during 1990-2008. However N_2O emission from wastewater is estimated 26% the total greenhouse gas emission (CO_2, CH_4 and N_2O) of the water chain, being the sum of drinking water production, water transport, wastewater and sludge treatment and discharge (Frijns *et al.,* 2008).

Nitrous oxide (N_2O) is a greenhouse gas with significant potency about 310 times heat trap ability of carbon dioxide. N_2O may be produced at low concentrations of oxygen that may be present in both anoxic and aeration tanks of biological nitrogen removal (BNR). The denitrification process may produce N_2O at low COD/N ratio in wastewater. For this reason, it is possible to find N_2O in an anoxic tank of BNR. However, the main microorganisms responsible for N_2O emission have not been definitively identified. Until now, in Thailand, there is never report of measure N_2O emission during BNR from the full scale WWTP. They always measure on lab scale. Thai pollution control department declares that oxide of nitrogen emission must measure according to USEPA method.

According to general method of N_2O emission measurement during BNR from WWTP should follow USEPA method. This method recommends that N_2O emission from WWTP should use the USEPA flux chamber or this chamber properly matches with the isolating flux chamber commercial sell at http://www.fivesenses.com. Due to the high cost and shipping, in this work, the flux chamber was developed in order to use at the onsite emission gas collecting chamber (OSEGCC).

The experiment was desired to float the OSEGCC in the large wastewater treatment plant in Bangkok for 24 hours to keep daily nitrous oxide emission gas in two zones, anoxic zone and aerobic zone of activated sludge biological nitrogen reactor in WWTP. Daily grab samples were delivery to the Environmental Research Training Centre, Rangsit Klong 5 in a few hours.

The OSEGCC is capable to collect N_2O gas from both anoxic and aeration tanks very well. The N_2O concentrations in anoxic and aeration tanks of biological nitrogen removal at the selected centralized WWTP in Bangkok were 25 and 17 ppm or 0.44 and 0.35% of nitrogen load or 0.00114 and 0.00079 g N/person/yr respectively.

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OBJECTIVES

The main objective of this research was to develop the tool to collect nitrous oxide (N_2O) from full scale of activated sludge wastewater treatment plant with biological nitrogen removal in Bangkok, Thailand. This tool was called the onsite emission gas collecting chamber (OSEGCC). The method of collecting N_2O emission sample and analysis of N_2O from WWTP was modified from the U4R07 protocol and based on appropriated technique in the field.

Scope of the study

1. To conduct by setting up the research which the developing OSEGCC floated by a wheel in anoxic zone and hang with the ceiling in an activated sludge (AS) with biological nitrogen removal (BNR) reactor operation in the selected centralized WWTP Bangkok Thailand. Collect emission gases 24 hours and then absorb collecting gas to the tedlar bag. After that grab samples were delivery to measure at Environmental Research Training Centre Rangsit Klong 5 Pratumthani right away.

2. To repeat the same process (1) but float the OSEGCC in aerobic zone on tomorrow.

3. To prove that the OSEGCC which was designed following the USEPA could be collected nitrous oxide emission.

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LISTERATURE REVIEW

1. Global Warming

The latest Intergovernmental Panel on Climate Change (IPCC) report indicates that global surface temperature will probably rise 1.1 - 6.4 °C during the twenty-first century. The global rising temperature will cause the rising sea level, changing the amount and pattern of precipitation , expansion of subtropical deserts ,the continuing retreat of glaciers, permafrost and sea ice ,the intensity of extreme weather events , species extinctions and changes in agricultural yields.

The IPCC concludes that increasing greenhouse gas concentrations resulting from human activities. The 6 gases which cause green house effect are carbon dioxide, methane, nitrous oxide, sulfur hexafluoride, CFCs and PCFs**.**

Nowadays, human is realized that he could not consume only energy. Floods, snow, storm, earthquake Tsunami and the extremely weather are worst experience them to consume the sufficiency energy and live friendly with the around environment. Human must concern in any activities to survive substantially. Moreover, human should start to find the way to protect the environment for our children in the future.

2. N_2O and the Environmental

Nitrous oxide is greenhouse gas which global warming potential (GWP) compared to carbon dioxide (CO_2) 310 times. Nitrous oxide also causes ozone depletion. The new study suggests that N_2O emission currently is the single most important ozone depleting substance emission and is expected to remain the largest throughout the 21st century.

N_2O is the laughing gas or anesthetic gas which uses in dental treatment, surgery in the hospital and popular use in the mobile acceleration. It comes from many human activities as the USEPA survey according to its source emission each year as shown in the Table 1

Table 1 US Nitrous Oxide Emissions by Source ($TgCO_2$ Equivalents)

Source Category	1990	1995	2000	2005	2006	2007	2008
Agricultural Soil Management	203.5	205.9	210.1	215.8	211.2	211.0	215.9
Mobile Combustion	43.9	54.0	53.2	36.9	33.6	30.3	26.1
Nitric Acid Production	18.9	21.0	20.7	17.6	17.2	20.5	19.0

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Table 1 US Nitrous Oxide Emissions by Source ($TgCO_2$ Equivalents) (continued)

Source Category	1990	1995	2000	2005	2006	2007	2008
Manure Management	14.4	15.5	16.7	16.6	17.3	17.3	17.1
Stationary Combustion	12.8	13.3	14.5	14.7	14.5	14.6	14.2
Acidic Acid Production	15.8	17.6	5.5	5.0	4.3	3.7	2.0
Wastewater Treatment	3.7	4.0	4.5	4.7	4.8	4.9	4.9
N_2O from Product Uses	4.4	4.6	4.9	4.4	4.4	4.4	4.4
Remaining Forest Land	2.7	3.7	12.1	8.4	18.0	16.7	10.1
Composting	0.4	0.8	1.4	1.7	1.8	1.8	1.8
Settlements Remaining	1.0	1.2	1.1	1.5	1.5	1.6	1.6
Field Burning of Agricultural Residues	0.4	0.4	0.5	0.5	0.5	0.5	0.5
Incineration of Waste	0.5	0.5	0.4	0.4	0.4	0.4	0.4
Wetlands Remaining	+	+	+	+	+	+	+
International Bunker Fuels	1.1	0.9	0.9	1.0	1.2	1.2	1.2
Total for US	**322.3**	**342.5**	**345.5**	**328.3**	**329.5**	**327.7**	**318.2**

Source: Environmental Protection Agency. 2012. **About Nitrous Oxide Emission and Source**. Available Source: http://www.epa.gov/nitrousoxide/sources.html, April 12, 2012

Mostly nitrous oxide comes from croplands contributed nearly 69% of total direct nitrous oxide (N_2O) emissions and the mention human activities. About 1.5 %

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of all occurs from wastewater treatment plants. However its trend growth seems to increase a further sharply.

3. Wastewater Treatment Process

There are three wastewater treatment processes.

3.1 Physical treatment process is the removal of wastewater constituents such as rags sticks floatables, grit and grease that may cause maintenance or operational problems with the treatment operations, processes and ancillary systems and also the removal of a portion of the suspended solids and organic matter from the wastewater.

3.2 Biological treatment process is the nutrient removal such as biodegradable organics, suspended solids, and nutrient (nitrogen)

3.3 Chemical treatment process is the removal of heavy metals such as phosphorus, zinc, sulfur and disinfection.

Source : Metcalf and Eddy, (2003).

4. Biological Nitrogen Removal in Municipal Wastewater Treatment Plant in Thailand

In Thailand, there are many kinds of BNR reactor in the biological treatment in municipal wastewater treatment plants. Some are contract stabilization, batch sequential reactor but they are mostly activated sludge. This research selects activated sludge reactor completely mixed wastewater treatment plant for sampling emission gas both in aerobic zone and anoxic zone

Source: Department of Drainage and Sewerage .2012.**About Municipal Wastewater Treatment plants Thailand,** Available source: http://dds.bangkok.go.th, March 5, 2012

5. The Nitrification and Denitrification Stoichiometric Equation

In Biological treatment process, the nitrification and denitrification process are occurred by microorganisms such as bacteria reacting with oxygen and without oxygen.

5.1 Nitrification involves the two step biological conversion of ammonia to nitrite and then to nitrate under aerobic condition. The conventions to nitrite and nitrate involve two specific groups of autotrophic bacteria such as nirosomonas and nitrobacteria. Autotrophic bacteria that consume organic material (BOD) in that chemoautrophic bacteria use carbon dioxide as their carbon source and specific inorganic chemicals as a source of energy for growth. In the case of nitrosamines and nitrobacteria, the inorganic chemicals used are ammonia and nitrite, respectively.

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The stoichiometric equation that defined the molar ratios for the oxidation of ammonium (NH_4^+) to nitrite (NO_2^-) by nitrosamines is the following;

$$NH_4^+ + 1.5\ O_2 \xrightarrow{\text{Nitrosamines}} NO_2^- + 2\ H^+ + H_2O + \text{Energy}$$

Similarly, the stochiometric equation that describes the oxidation of nitrite to nitrate by Nitrobacteria is the following;

$$NO_2^- + 0.5\ O_2 \xrightarrow{\text{Nitrobacteria}} NO_3^- + \text{Energy}$$

The overall stoichiometric expression for the two step nitrification process as follows:

$$NH_4^+ + 2O_2 \longrightarrow NO_3^- + 2H^+ + H_2O + \text{Energy}$$

Along with obtaining energy, some of ammonium ion is assimilated into cell issue

$$4CO_2 + HCO_3^- + NH_4^+ + H_2O \longrightarrow C_5H_7O_2N + 5O_2$$

The overall oxidation and synthesis reaction can be represented as follows:

$$NH_4^+ + 1.83\ O_2 + 1.98\ HCO_3^- \longrightarrow 0.02\ C_5H_7O_2N + 0.98\ NO_3^- + 1.041\ H_2O + 1.88\ H_2CO_3$$

5.2 Denitrification biological denitrification occurs naturally when certain bacteria use nitrate as terminal electron acceptor in their respiratory process, in the absence of oxygen. Denitrification consists of a sequence of enzymatic equation reaction leading to the evolution of nitrogen gas. The process involves the formation of a number of nitrogen intermediates and can be summarized as follows.

$$NO_3^- \xrightarrow{\text{Denitrification bacteria}} NO_2^- \longrightarrow NO \longrightarrow N_2O \longrightarrow N_2$$

Or

$$NO_3^- + H^+ + 5e^- \longrightarrow \tfrac{1}{2}\ N_2 + 3H_2O$$

Elemental nitrogen is the end product of this process. But intermediate accumulation of nitric oxide and nitrous oxide may take place under certain condition (Korom, 1992).

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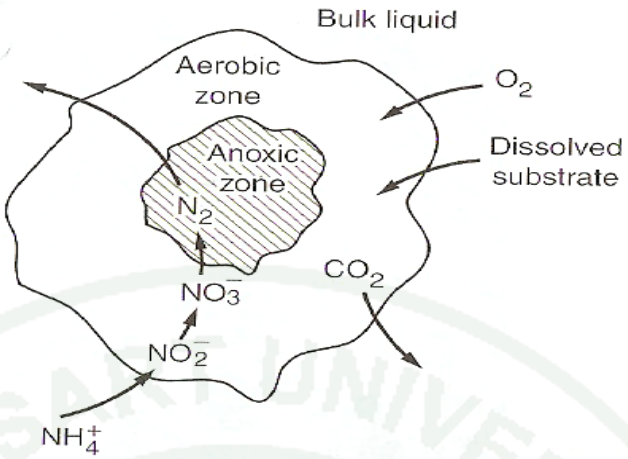

Figure 1 Diagram of an activated sludge particle showing aerobic and anoxic zones

Source : Metcalf and Eddy (2003)

6. The Standard Nitrous Oxide Emission Limit from Wastewater Treatment by IPCC in 2006

N_2O is produced by microorganism such as bacteria nitrification and denitrification from biological nitrogen removal treatment in wastewater treatment. Its emissions are from the several processes in wastewater treatment plants and the emission fluxes are extremely variable and depend on many operational parameters.

The water board apply the IPCC guide line that estimation of the N_2O emission from WWTPs (IPCC, 2006). The IPCC specifics that for countries with advanced centralized WWTP, the nitrous emission from WWTP is 3.2 g N/person/year, corresponding to approximately 0.035% N_2O emission of the nitrogen load of a WWTP. The factor of 3.2 g N_2O N/person/year is based on one study in one small BOD removal WWTP (Czepiel *et al.,*1995).

N_2O emission from wastewater is estimated to contribute 26% to the total greenhouse gas emission (CO_2, CH_4 and N_2O) of the water chain, such as the sum of drinking water production, water transport, wastewater and sludge treatment and discharge (Frijns *et al.,* 2008).

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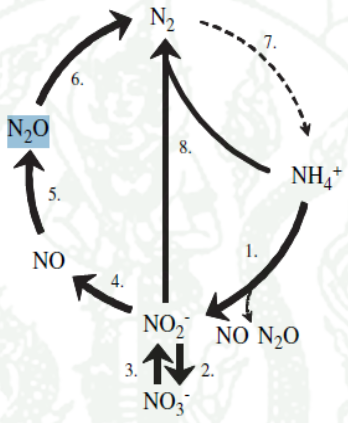
7. Biological Nitrogen Conversions

Nitrogen, generally present in wastewater in reduced form as ammonium, is removed during conventional wastewater treatment by two sequential biological processes: nitrification and denitrification.

During nitrification ammonia is converted into nitrite or nitrate, which is subsequently reduced to emission nitrogen oxides. It is identified that the biological processes and key process conditions that are responsible for N_2O emission.

From Figure 2 NH_4^+ will be oxidized to nitrite by autotrophic and heterotrophic AOB and AOA or called aerobic ammonia oxidation in state1. Then nitrite is oxidized or electron reduction to nitrate in state 2 by NOB called aerobic nitrite oxidation the other states shown name state relevant to reduction oxidation reaction and the microorganism names



(1) Aerobic ammonia oxidation (autotrophic and heterotrophic AOB and AOA,
(2) Aerobic nitrite oxidation (NOB),
(3) Nitrate reduction to nitrite (DEN),
(4) Nitrite reduction to nitric oxide (AOB and DEN),
(5) Nitric oxide reduction to nitrous oxide (AOB and DEN),
(6) Nitrous oxide reduction to dinitrogen gas (DEN),
(7) Nitrogen fixation (not relevant in most WWTPs),

Figure 2 Biological Nitrogen Conversions

Source : Kampschreura *et al.*, (2009).

Nitrous oxide, a potent greenhouse gas, can be emitted during wastewater treatment, significantly contributing to the greenhouse gas footprint. Measurements at lab scale and full scale wastewater treatment plants have demonstrated that N_2O can be emitted in substantial amounts during nitrogen removal in WWTPs. However, a large variation in reported emission values exists. Analysis of data enabled the identification of the most important operational parameters leading to N_2O emission in WWTPs.

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(1) low dissolved oxygen concentration in the nitrification and denitrification stages.

(2) increased nitrite concentrations in both nitrification and denitrification stages.

(3) low COD/N ratio in the denitrification stage.

From the literature review it remains unclear whether nitrifying or denitrifying microorganisms are the main source of N_2O emissions.

Operational strategies to prevent N_2O emission from WWTPs are discussed and areas in which further research is required are identified (Kampschreura *et al.*, 2009).

8. N_2O Emissions from Full Scale and Lab Scale WWTPs

Several studies on N_2O emission from WWTPs have been performed. Emission data show a huge variation in the fraction of nitrogen that is emitted as nitrous oxide, both in lab scale (0–95% of the nitrogen load) and full-scale (0–14.6% of the nitrogen load) studies. (Kampschreur *et al.,* 2009)

In Thailand, the research which measured GHGs such as CO_2 CH_4 N_2O from construction wetland by closed flux chamber, the result could measure only CO_2 CH_4 but could not measure N_2O cause of the little ORP reason. (Wicramarachchi, 2008).

9. N_2O is Emitted from Compartments in WWTP

Since N_2O is produced during nitrification and denitrification, the production of N_2O mainly occurs in the activated sludge biological nitrogen remover units of a WWTP.

It is possible locations where N_2O emission can occur are grit tanks, pre-sedimentation tanks, secondary clarifiers, sludge storage tanks and anaerobic sludge digesters anywhere there are nitrification and denitrification. N_2O emission from these compartments can only occur by nitrification if oxygen can penetrate the system which only occurs in the grit tanks in small quantities and by denitrification if nitrite or nitrate is present for well managed plants for nitrogen removal this should not occur at large quantities in any of the mentioned compartments.

Measurements at one WWTP indicate that 90% of the N_2O emission occurs from the activated sludge compartments, 5% from the grit tanks and 5% from the sludge storage tanks by (Czepiel *et al.* 1995).

10. Main Parameters Lead to N_2O Emission

Figure 3 is shown the main parameter leads to N_2O emission in nitrification tank such as (1) insufficient aeration (low oxygen) , (2) high nitrite (high toxic, low temperature , high ammonia concentration) , and in denitrification tank (3) high oxygen (over aeration in nitrification stage) (4) high nitrite (nitrite transfer denitrification stage) (5) low COD/N

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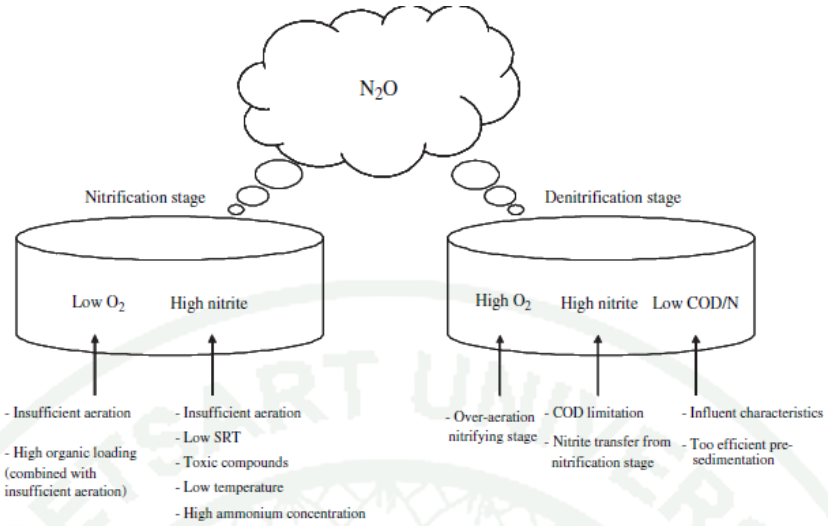

Figure 3 Main parameters lead to N_2O emission

Source : Kampschreura *et al.*, (2009).

The tendency of WWTPs to decrease their energy consumption by decreasing aeration could be adverse towards the greenhouse effect, even though it decreases CO_2 emission, this could be counteracted by the increased N_2O emission due to its 300 fold stronger greenhouse effect.

Rapidly changing process conditions lead to increased N_2O emission. There are indications that growth on internal storage compounds can lead to N_2O emission, but the mechanism is unclear, scientific findings are contradictory (Kampschreura, M.J. *et al.* , 2009).

11. Gas Sampling Method

There are many kind of sampling gas methods. In Thailand, gas sampling keeping always absorb the sampling gases from an investigating location to a tedlar bag or a tank to measure by GCMS, GC detector type ECD. That is not the real gas concentration because of its diffusion. Sometimes there are gas monitoring stations and the analytical measurements such as TELEDYNE, ECOTECH are provided. But its sampling is not by close flux chamber. It is measured by sampling mention above which result will be less than real concentration.

11.1 Gas Collector

In Taiwan ,The samples were collected in the 11 tedlar bags with a single polypropylene fitting This fitting contained a Teflon syringe port lines septum and a Teflon syringe port lined septum and a hose connection, which functioned as shut off valve for incoming and outgoing gas meanwhile, a 500 ml gas collector (GL sciences Inc., Tokyo, Japan) was used to withdraw gas samples from the biogas outlets of covered anaerobic wastewater treatment basins and the exhausting outlets of a close

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composting house. All gas samples were collected every 2 weeks for GC analysis (Su *et al.*, 2003).

11.2 Closing Chamber Made of PMMA (polymethyl methacrylate)

It was used to stock gas in a wetland. When sampling, the chamber was placed on the sand to ensure gas samples to be well mixed, air inside the chambers was circulated with battery driven fans during the measurement. The closing chamber which was made of PMMA is shown in Figure 4

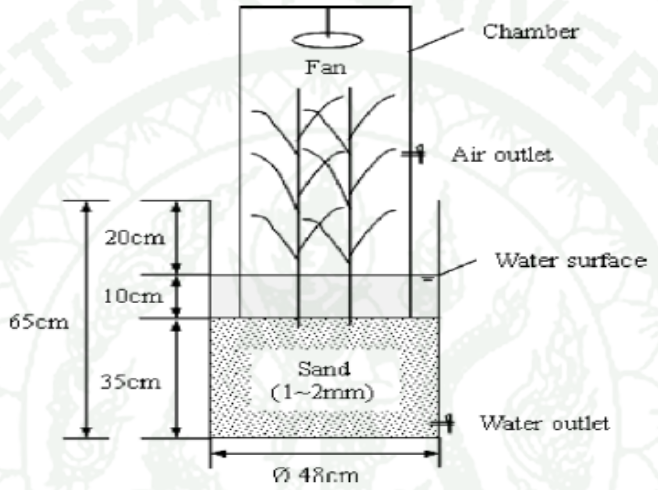

Figure 4 Closing chamber made of PMMA (Polymethyl Methacrylate)

Source: Wu and Zhang (2009)

11.3 The Surface Emission Isolation Flux Chamber (SEIFC)

Commercially available replicas of the USEPA surface emission isolation flux chamber (SEIFC). Figure 5, can be used to measure gaseous N fluxes from activated sludge reactors. The SEIFC consists of a floating enclosed space from which exhaust gas is collected in a real time or discrete fashion. Since the surface area under the SEIFC can be measured, the specific flux of the gaseous compound of interest can be indirectly determined. The SEIFC 'floats' on the activated sludge tank surface and several replicate measurements can be taken at different locations in a single tank as well as from different tanks (nitrification, denitrification) along a treatment train.

The SEIFC is also equipped with mixing (physical mixer or via sweep gas circulation) to ensure adequate gas and in some cases, an online temperature probe. The SEIFC is currently one of the few devices accepted by the USEPA for measuring gaseous fluxes. In general, gases sampling will be conducted at multiple locations of the activated sludge train in each wastewater treatment facility. These locations are the aerobic, anoxic zones, depending upon the configuration of the given facility.

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Figure 5 Surface emission isolation flux chamber (SEIFC)

Source : Fivesenses. 2012. **About Surface Emission Insulating Flux Chamber.** Available Source : http://www.fivesenses.com, March 5, 2012.

11.4 The Isolating Emission Flux Chamber Taking Stock of Nitrous Oxide

Professor Dr. Kartik Chandran associated with WERF presently distributes this isolating emission flux chamber to which WWT plant is interested to cooperate this project , support funds for WERF. The isolating emission flux chamber taking stock of N_2O is shown in Figure 6 and the calculating nitrogen emission formula would be delivered to WWTP.

Biological nutrient removal operations can lead to significant emissions of nitrogen greenhouse gases such as nitrous oxide and the reactive nitrogen compounds nitric oxide and nitrogen dioxide.

Researchers are collecting full scale data for nitrous oxide measurement and surface emission isolation flux chambers. They have identified principal aqueous and gaseous intermediates in activated sludge tanks operated under different configurations, nitrogen loads, and dissolved oxygen concentrations.

In addition to developing an inventory of releases and strategies to limit those releases, this project is characterizing nitrogenous green house gas emissions from wastewater treatment plants (Chandran, 2011).

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Figure 6 The isolating emission flux chamber taking stock of nitrous oxide

Source: Chandran (2011).

11.5 The developed onsite emission gas collecting chamber and the sampling method under USEPA

In 2009, The author had gotten the U4R07 protocol directly from Professor Dr. Kartik Chandran via email. The protocol was being the absence of approach by USEPA. The protocol was for nitrogen greenhouse gas emissions online monitoring. So he advised that, if it was hard to find analytical instrument like TELEDYNE 320 API monitor in Thailand, the grab samples should be applied. Helium gas is too expensive to be sweep gas so zero air could be used. However , The SEIFC is presently already USEPA approved. In 2012, Professor Dr. Kartik Chandran was admired to be the important person. In USA ,The protocol U4R07 measuring nitrous oxide emission from wastewater treatment plant was already approved by USEPA and used across the US for nitrous oxide measurement.

Source: Biodieselmagazine. 2012. **About Nitrous Oxide (N_2O) Emissions at Wastewater Treatment Facilities, Chandran, Approved by USEPA**. Available source: http://www.biodieselmagazine.com/articles /7873 , April 16, 2012

Since the author has developed the close flux chamber which was replica of the SEIFC. The developed onsite emission gas collecting chamber would accepted the by USEPA also. The simple design of USEPA flux chamber for WWTP was the close flux chamber which shall be floated on the wastewater surface, the bottom rim of the chamber must minimum be in 1-2 inch wastewater. And the close flux chamber, conduit should use the matter which is opposite with sampling gases.

The sampling method which was applied to be grab samples, sampling procedure was still acted under the U4R07 protocol. Consequently, the sampling method in this research was done under USPEA.

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12. U4R07 Protocol: Characterization of Nitrogen Greenhouse Gas Emissions from Wastewater Treatment BNR Operations

The push to achieve greater nitrogen removal from wastewater treatment plants, while minimizing infrastructure investments and operating costs, has resulted in the development of a wide range of innovative biological nitrogen removal processes. However, BNR strategies could be a significant contributor to atmospheric and NO depending upon the reactor configurations and operating conditions. In the future, as BNR is implemented at wastewater treatment plants around the nation, the flux of these gases to the atmosphere could significantly increase. Such increased releases would be a major concern since the greenhouse impact of nitrous oxide is about three hundred times that of carbon dioxide. Furthermore, nitric oxide is converted to nitrogen dioxide in the atmosphere, which is a precursor to photochemical smog (ozone).

The project description , standardization of overall N-GHG measurement methodology ,material equipment tool needed, sampling gas in an aerobic and an anoxic zone which relevant to this work cut to this review literature as the guide of the more study in the future.

12.1 Project Description

The goal of this WERF project is to characterize nitrogenous emissions from the activated sludge portion of wastewater treatment plants. This project represents one of the first attempts at characterizing nitrogenous GHG emissions from wastewater treatment plants, and developing a methodology for collection of full scale plant data from a range of nutrient removal facilities in the United States.

Building on previous work by the project team, this information will be integrated into an activated sludge model 1 based mechanistic process model, which will be refined through this project through the addition of autotrophic pathways for and nitric oxide emission. The refined mechanistic model will allow the industry to codify the results of this research, and develop a tool that will aid in the prediction and therefore mitigation of nitric oxide and emissions from WWTPs utilizing a range of wastewater treatment processes. Ultimately, this could allow the wastewater sector to engineer strategies for wastewater treatment that minimize gaseous nitrogen oxide emissions

12.2 Standardization of Overall N GHG Measurement Methodology

The overall procedure for measuring, NO and fluxes from the head-space of activated sludge tanks involves a variant of the EPA/600/8-86/008 and the SCAQMD tracer methods. Gas phase analyses will be conducted via infra-red (N_2O) and chemiluminescence (NOx) analyzers.

In 2009, this protocol is the absence of an approved (USEPA or ASTM) method for N_2O in air or water, method modification was necessary to meet project objectives and measure N_2O emissions. To evaluate the performance of the measurement of , NO and fluxes using the procedure developed by the researchers, three side-by-side monitoring events were conducted along with the research

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procedure during the first sampling event at a step feed BNR facility. In addition to the research protocol performed by Columbia University staff, two additional side-by-side monitoring events were conducted as follows:

Plant wastewater research engineers measured fluxes using the EPA isolation flux chamber and SCAQMD tracer method but with a photo acoustic analyzer to directly determine N_2O.

Chuck Schmidt, Ph.D. used the textbook EPA isolation flux chamber and SCAQMD tracer dilution method to measure the flux and the following analytical methods to measure ozone precursors and GHGs.

12.3 The SEIFC

The SEIFC is currently one of the few devices accepted by the USEPA for measuring gaseous fluxes and as such will be employed for this study

12.4 Sampling Design for Full Scale Monitoring

In general, sampling will be conducted at multiple locations of the activated sludge train in each wastewater treatment facility. These locations the aerobic, anoxic zones, depending upon the configuration of the given facility. Full scale measurement of gas fluxes will be conducted at different locations along the activated sludge train at each full scale wastewater treatment facility. Based on a fundamental understanding of the biological pathways that contribute to fluxes from activated sludge, the transition between the aerobic and anoxic zones is expected to be point contributing most to these fluxes.

Nevertheless, at each plant, NO and emissions will be monitored from anoxic and aerobic zones. Typically, we anticipate sampling at one point in each anoxic zone and each aerobic zone with active nitrification along the treatment train.

During the course of the gas phase sampling, liquid phase samples will be collected adjacent to the hood location. The samples will be filtered immediately upon collection in the field and analyzed by host plant personnel for ammonia, nitrite and nitrate concentration, utilizing readily available field methods. As the primary purpose of these measurements is to ensure the presence of the targeted nitrogen species, without consideration to accuracy in the concentration measurements, the simplest available field method will be used for these preliminary measurements. Profiles of the nitrogen species along the aeration tank will be collected using the plants standard sampling and analysis procedures.

12.5 Measuring the Surface Flux of Nitrous Oxide and Nitric Oxide from Activated Sludge Tanks

The following protocol, which has been prepared as part of this project, is intended to provide utilities and field sampling teams with a detailed description of the data collection methodology and analysis requirements to enable calculation of gaseous nitrogen fluxes from different zones of activated sludge trains in a wastewater treatment facility.

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12.6 Equipments, Materials and Supplies

12.6.1Surface emission isolation flux chamber (commercially available from vendors, for instance, http://www.fivesenses.com/Prod_Emission.cfm or custom built based on specifications from the United States Environmental Protection Agency

12.6.2 Teledyne API Monitor Model 320E

12.6.3 Ecophysics NOx Analyzer Model CLD64

12.6.4 Zero gas (containing zero ppm and NO), and and NO gas standards

12.6.5 Dwyer series 475 Mark III digital manometers to measure flux chamber pressure from 0 to 1" and 0 to 100" of water column

12.6.6 Rotameter to measure influent sweep gas flow rate, 0 - 30 L/min

12.6.7 Adjustable air pump, 0-10 L/min to provide sweep gas flow into the flux chamber

12.6.8 Vacuum pump, 0-30 L/min for active pumping of gas from the flux chamber (never required based on sampling campaigns conducted to date)

12.6.9 0.2 μm cartridge filters, set of 10 to prevent fine particulates from entering the gas analyzers

12.6.10 Silica Gel column for capturing moisture

12.6.11 Glass water trap consisting of a 100 ml glass bottle placed in ice within a Styrofoam box

12.6.12 Teflon tubing (approximately 0.5") and fittings

12.6.13 100-300' extension cord and power strip

12.6.14 Laptop personal computer (with at least 512 MB RAM) with data acquisition programs for and NOx analyzers pre installed

12.6.15 Set of miscellaneous hand-tools including adjustable wrenches, different size screw drivers and adjustable pliers.

12.7 Experimental Procedure

NO and fluxes from the head space of activated sludge tanks involves a variant of the EPA/600/8-86/008 and the SCAQMD tracer methods, which allow sampling of gaseous emissions from high surface flux rate operations. The USEPA SEIFC essentially consists of a floating enclosed space through which carrier gas is fed at a fixed flow rate and exhaust gas is collected in a real time or discrete fashion. Since the surface area under the SEIFC can be calculated or measured, the specific flux of the gaseous compound of interest can thus be determined. Since the SEIFC floats on the activated sludge tank surface, several replicate measurements can be taken at different locations in a single tank as well as from different tanks (nitrification, denitrification) along a treatment train. The SEIFC is also equipped with mixing to ensure adequate gas and in some cases, an online temperature probe. The SEIFC is currently one of the few devices accepted by the USEPA for measuring gaseous fluxes , in Figure 7

In general, sampling will be conducted at multiple locations of the activated sludge train in each wastewater treatment facility. These locations the aerobic, anoxic are depending upon the configuration of the given facility. Additionally, within each zone, multiple points will be sampled to address any variability in gas fluxes that may result due to variations in mixing or flow patterns therein.

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Pressure build up can be minimized by equipping the flux chamber with multiple vents or a variable size vent and continuously monitoring the pressure drop across the hood using a sensitive pressure gauge. In this study, the latter approach (pressure gauge) will be followed to monitor the pressure across the flux chamber. The modified set up of the flux chamber used in this study is depicted in below Figure 8

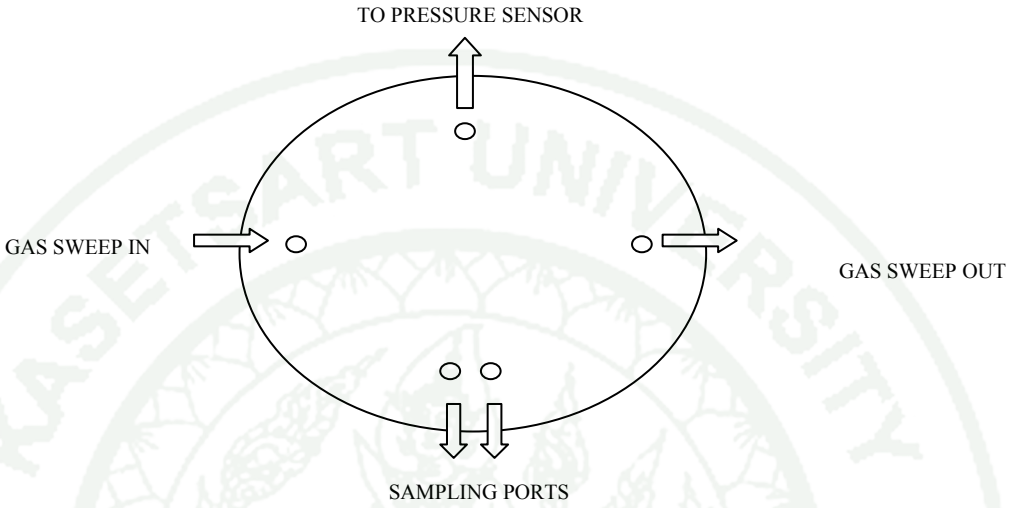

Figure 7 Modified schematic of the flux chamber

Source : Chandran (2009).

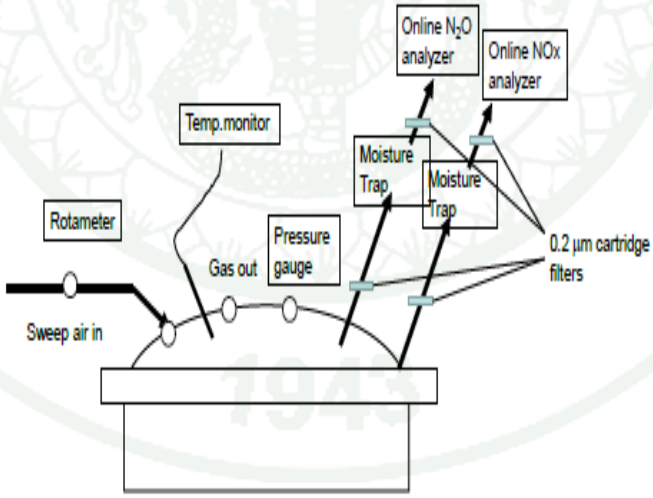

Figure 8 Schematic of flux chamber set up for N_2O and NO_x flux measurements

Source : Chandran (2009).

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12.8 Gas Sampling Method in Aerobic Zones

12.8.1 Seal all but one vent in the flux chamber and connect high sensitivity pressure gauge to the one open vent.

12.8.2. Lower flux chamber into aerobic zone (bottom of rim should be below the surface of the water by 1-2 inches minimum).

12.8.3 Wait for analyzer to equilibrate based on stability indicator (<0.03)

12.8.4 Pull the flux chamber up. Open two vents and connect the analyzer, NOx analyzer. The other vents should be left open to atmosphere.

12.8.5 Record temperature of the gas in the flux chamber using a digital temperature gauge.

12.8.6 Care must be taken not to have the flow going to the two analyzers exceed the gas flow rate from the flux chamber. Otherwise, atmospheric air will be drawn in through the vents in the flux chamber

12.9 Gas Phase Sampling Method in Anoxic Zones

12.9.1 Seal all but one vent in the flux chamber and connect high sensitivity pressure gauge to the one open vent.

12.9.2 Lower flux chamber into anoxic zone with a (1-2 inch minimum submergence, into the liquid surface)

12.9.3 Wait for N_2O analyzer to equilibrate based on stability indicator (<0.03)

12.9.4 Pull the flux chamber up. Open two vents and connect the analyzer, NO_x analyzer and the sweep gas pump (Note: sweep gas only used during anoxic zone sampling). The other vents should be left open to atmosphere.

12.9.5 Record temperature of the gas in the flux chamber using a digital temperature gauge.

12.9.6 Care must be taken never to have the flow going to the two analyzers exceed the sweep gas rate or dilution air will be drawn in through an opening in the chamber.

12.10 Determination of Fluxes

Calculation the net flux of gaseous N species (mg/min) based on the gas flow rate out of the flux chamber (L/min) ,gas concentration (ppm) and the cross sectional area of the SEIFC (Equation 1)

$$\text{Flux} = \frac{Q_{\text{emission}} * C}{A} \quad (1)$$

Correct the calculated flux reflect standard temparature and pressure at 1 atm

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12.11 Determine of the lumped emission factor

Lumped emission factors for each facility will be computed based on the measure flux from each zone in the facility normalized to the daily influent total Kjeldahl nitrogen (TKN) loading (mass/mass) accroding to equation 2

$$\text{Emission factor} = \frac{\sum \text{flux} * \text{area (kg-N2O-N)}}{\text{Daily influent TKN Load (kg-N)}} \quad (2)$$

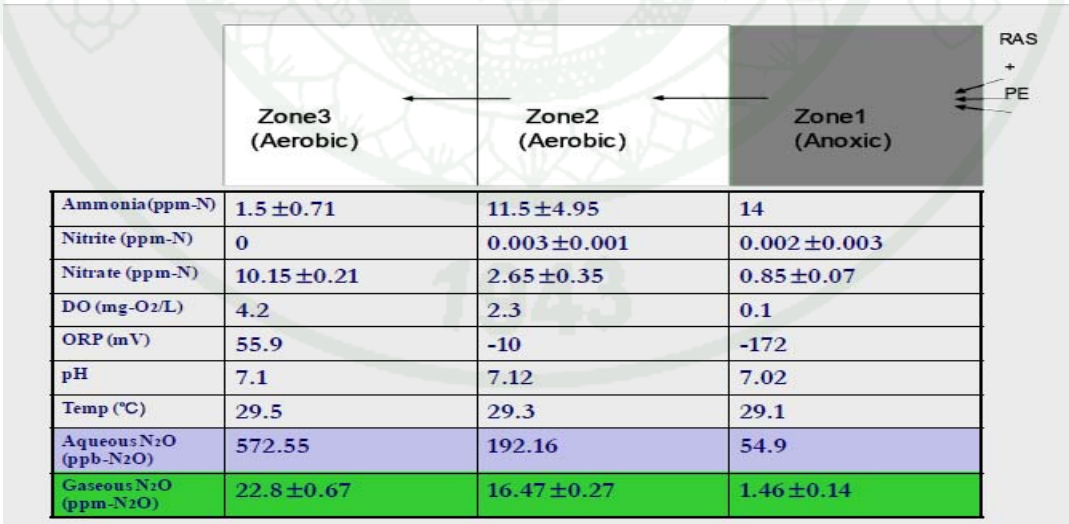
Flux = emission flux calculated from the zone (kg-N/d)

Area = surface area of the zone (m^2)

N = number of the zone

In Figure 9 is shown that The SEIFC and the protocol U4R07 can measure nitrous oxide emission from the large 1,000 million gallon per day of the wastewater treatment plant in Newyork USA. The N_2O results show 1.46 ppm in anoxic zone which is forecast that it is the main cuase of N_2O emission less than in arobic zone (22 ppm), It implies that The anoxic zone where the oxygen is absent is not the main source of nitrous emission as the previous researches

In Figure 10 is shown daily load charesteristic of ammonium gas and the biological nitrogen conversions cuases the hourly emission gases such as N_2O,NO_x in 1,000 million gallon per day of the wastewater treatment plant in Newyork USA.



	Zone3 (Aerobic)	Zone2 (Aerobic)	Zone1 (Anoxic)
Ammonia (ppm-N)	1.5 ±0.71	11.5 ±4.95	14
Nitrite (ppm-N)	0	0.003 ±0.001	0.002 ±0.003
Nitrate (ppm-N)	10.15 ±0.21	2.65 ±0.35	0.85 ±0.07
DO (mg-O_2/L)	4.2	2.3	0.1
ORP (mV)	55.9	-10	-172
pH	7.1	7.12	7.02
Temp (°C)	29.5	29.3	29.1
Aqueous N_2O (ppb-N_2O)	572.55	192.16	54.9
Gaseous N_2O (ppm-N_2O)	22.8 ±0.67	16.47 ±0.27	1.46 ±0.14

Figure 9 Significantly higher N_2O generation and emission in aerobic zone than anoxic zone

Source : Chandran (2009).

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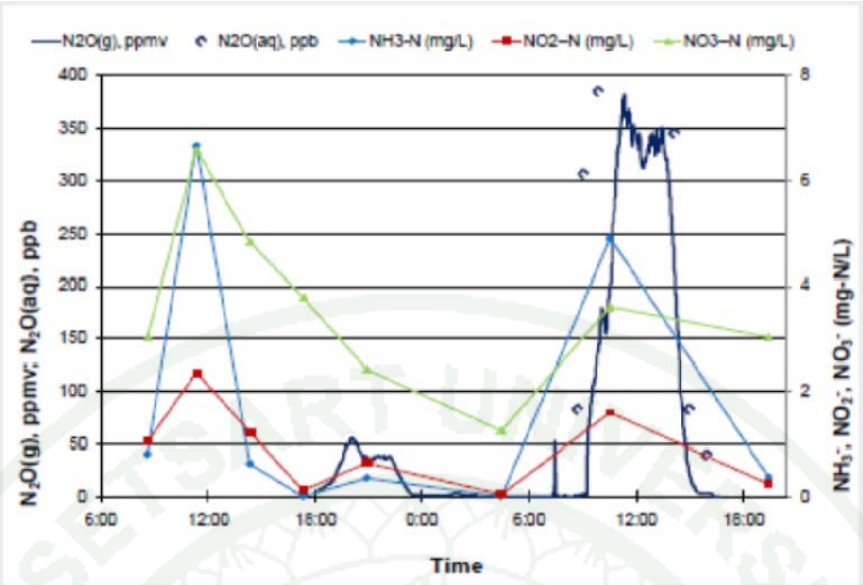

Figure 10 Hourly N_2O, NO_2 generation and emission related to NH_3-N

Source: Chandran (2009)

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MATERIALS AND METHODS

Materials

1. The Onsite Emission Gas Collecting Chamber Construction Design

Due to the high cost and shipping of the surface emission isolating flux chamber (SEIFC). In this work, the flux chamber was developed in order to use at the onsite emission gas collecting chamber (OSEGCC). Its weight is 2 kg to carry easily and its shape is cylindrical which is high 0.3048 m, diameter 0.3048 m and it can be hang with the ceiling or ladder. The OSEGCC was designed to collect gas on surface wastewater of WWTP without electricity requirement. To avoid sinking in the 7 m depth WWTP during gas collection, the OSEGCC was embraced with 0.3048 m inside diameter wheel operated by sliding it up or down with the level of the OSEGCC bottom rim which would be sunk in the wastewater. The OSEGCC was made of acrylic glass because it was quite clear. At least 10 L volume of headspace chamber was designed to collect sampling gas. The cylindrical chamber volume was totally 21 L because the design research intends to float the chamber which conducts the 14 L head space volume for big volume 10 L grab samples cause of low concentration nitrous oxide emission assumption. Open the OSEGCC two ports, one port is for gas input, another port is for gas output. And the ports are welded by the 4.55 m teflon conduits diameter ¼ inch as shown in Figure 11

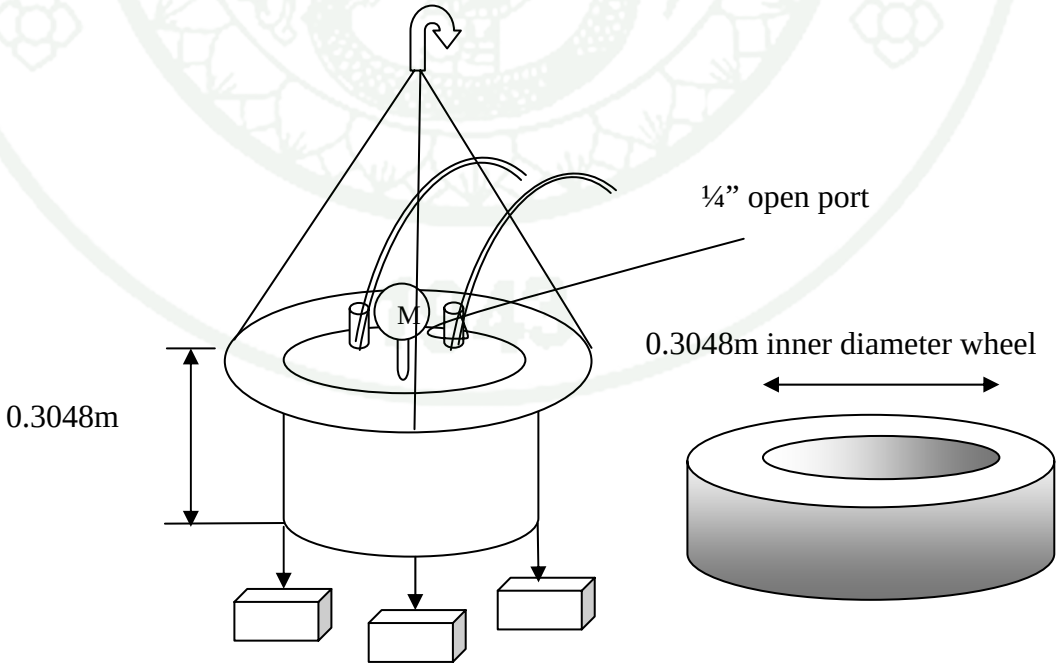

Figure 11 The onsite emission gas collecting chamber construction design

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2. Materials, Tool, Equipment and Instrument

In this work, the materials were used for the OSEGCC construction and the air absorbent pump 500 ml/min and the gas chromatography would be used to absorb and measure sampling gas listed below.

1. A wheel inside diameter 0.3048 m
2. Cylindrical acrylic glass outside diameter 0.3048 m , height 0.3048 m
3. Teflon conduit 10 m
4. Clear Silicone
5. Silica gel
6. Zero air tank , small size 10.5 Kg 150 Psi
7. Tedlar bag 10 L
8. Air absorbent pump 500 ml/min
9. A ladder
10. GCMS Agilent Technologies, 7890A
11. Nitrous oxide standard gas 100 ppm It would be diluted to be ppb depend on the real concentration of sampling gas.

3. Construction

1. Construct the OSGECC diameter 0.3048 m high 0.3048 m.
2. Embrace the OSEGCC with 1'diameter wheel.
3. Connect the two Teflon conduits diameter ¼ inch length 4.55 m. One port is for zero air flow in the OSEGCC, The other one port is connected with silica gel tube for air flow out the OSEGCC absorbed by air pump to 10 L tedlar bag.

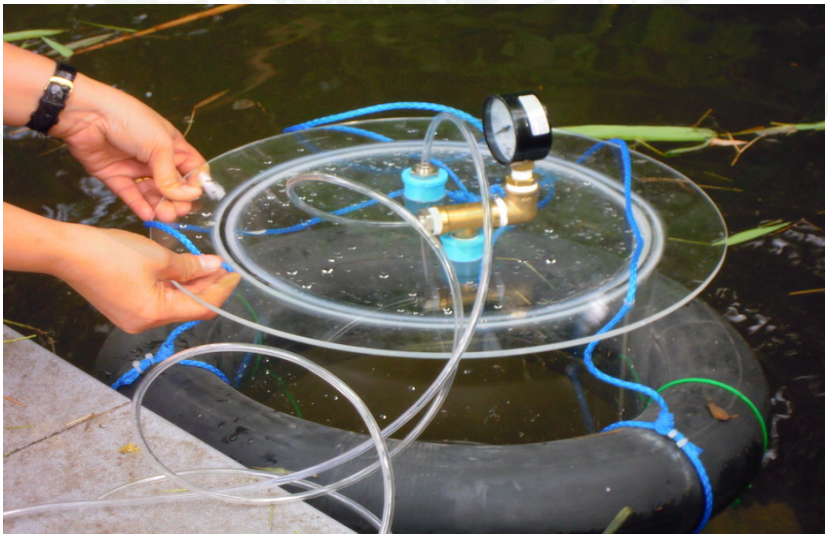

Figure 12 The onsite emission gas collecting chamber after construction

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Methods

The test experiments were conducted in the canal at SAMWA district, CUBON road to check whether the OSEGCC is leakage. Then it was check whether it could transfer gas from the OSEGCC to the tedlar bag after we put inflow zero air to it while it was absorbed the gas output by air absorbent pump rate 500 ml/min

1. Test leakage of the OSEGCC Test the OSEGGC whether it can stock gas when it was floated in the canal as shown in Figure 13

1. Light the aroma joss stick floated inside the OSEGCC 5 minutes.
2. Notice whether there is white smoke flow out of the OSEGCC

Figure 13 Test leakage of the onsite emission gas collecting chamber

2. Test transfer of the OSEGCC

Since the teplon long conduit is 4.55 m length. Therefore the pressure flows through the long conduits are drop. So the white smoke can not flow into the tedlar bag without air pump flow rate 500 ml/min as shown in Figure 14

1. Absorb white smoke from the OSEGCC by the air pump flow rate 500ml/min.
2. Notice whether there is white smoke flow in the 10 L tedlar bag

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Figure 14 Test transfer of the onsite emission gas collecting chamber

3. The pilot research

3.1 The design experiment would be conducted on both an aerobic and anoxic zone of completely mix activated sludge reactor in wastewater treatment plant Bangkok Thailand. Figure 15 is shown below

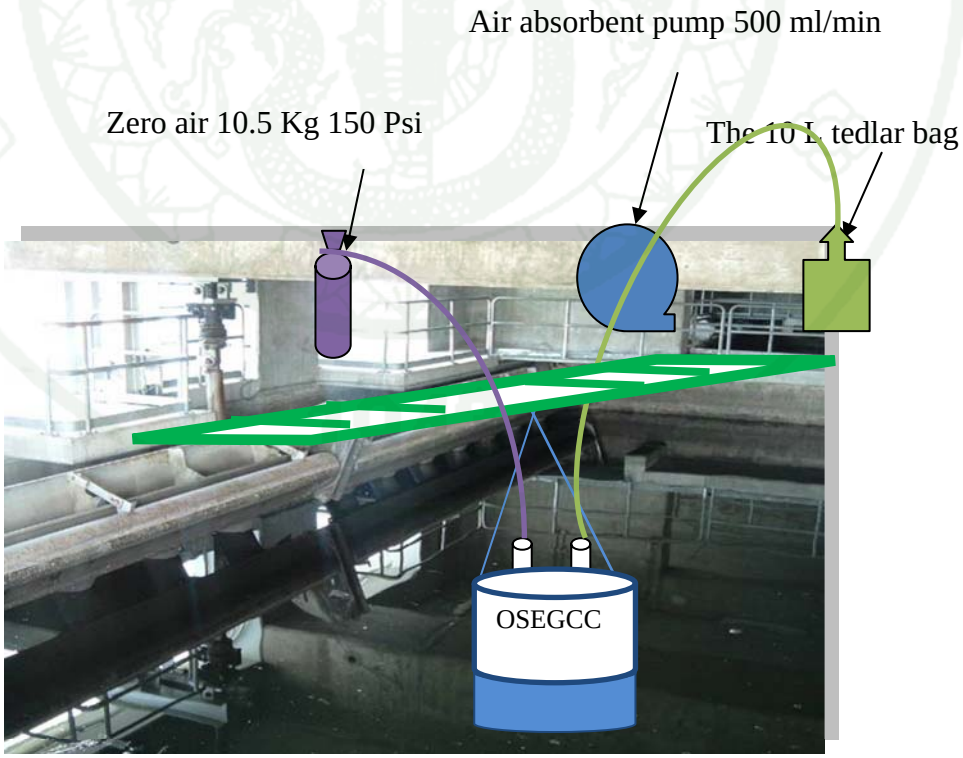

Figure 15 The experiment design of sampling nitrous oxide emission in anoxic zone and aerobic with biological nitrogen removal in the WWTP Bangkok

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3.2 Sampling Method in Anoxic and Aerobic Zone of Activated Sludge with BNR process

3.2.1. Hang the OSEGCC with the ladder which is on the calling slacks, weight the 3 concrete boxes to fix the OSEGCC, to avoid it swing and flow with the wastewater flow and the aerator run. The wheel is slide for floating the OSEGCC which the bottom rim would be sink in wastewater 4 inch in aerobic zone of activated sludge with biological nitrogen removal process

3.2.1.1 Put zero Air to force flow in the OSEGCC to clean dirty gases from it to tedlar bags (close system) after the OSEGCC is float on wastewater surface.

3.2.1.2 Collect nitrous oxide emission 24 hours

3.2.2 Absorb collecting gas by air pump to a tedlar bag about 10 L

3.2.3 Repeat the experiment in an anoxic zone of AS with BRN process

3.2.4 Measure the concentration gas by GCMS at the Environmental Research Technology Center Laboratory Rangsit Klong 5

The pilot researches had been done on the centralized wastewater treatment plant in Bangkok Thailand as shown in Figure 16-26. It was conducted on the 19 September 2011 in anoxic zone and the 20 September 2011 in aerobic zone.

Figure 16 The OSEGCC was hung with the ladder which was on the ceiling

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Figure 17 The OSEGCC was weighted with a few concrete boxes to protect turn over due to the aerator flow

Figure 18 The pilot scale was conducted in the anoxic zone of activated sludge with BNR process in full scale WWTP

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Figure 19 Personal Protection Equipment (PPE) was used in this experiment

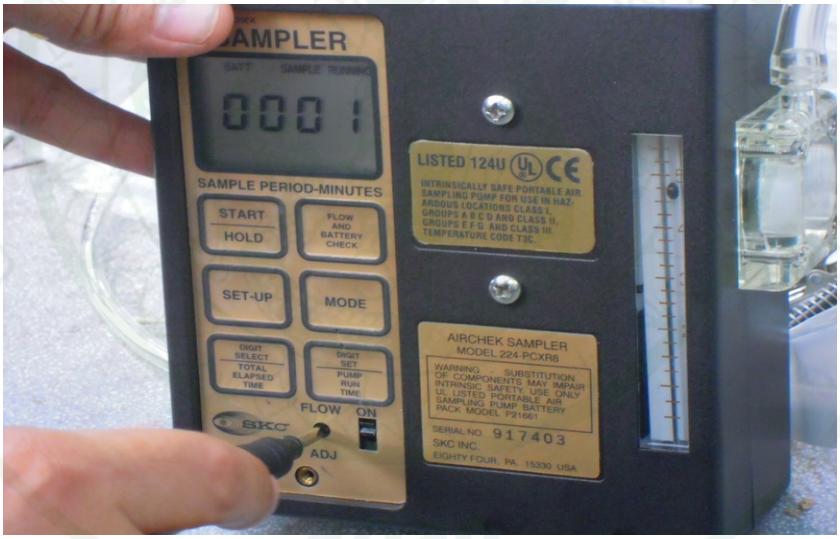

Figure 20 Air absorbent pump flow 100-500 ml/min

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Figure 21 Gas flow regulator

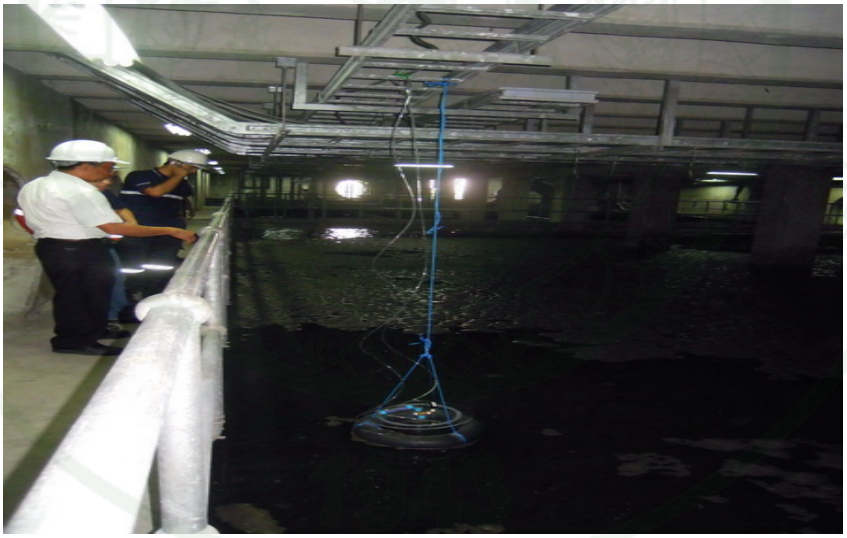

Figure 22 The OSEGCC was swung by aeretors in an aerobic zone**,** the three concrete boxes were wieght to protect its turn over

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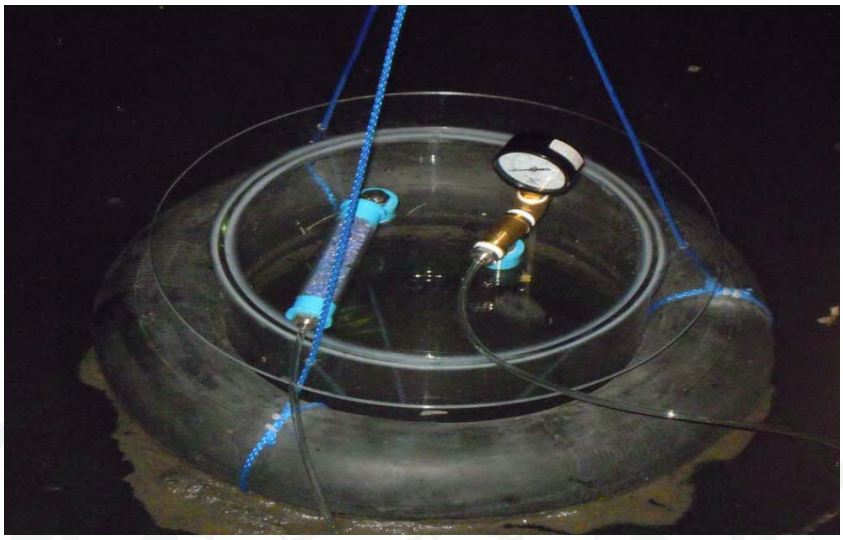

Figure 23 The OSEGCC with pressure gauge and siliga gel tube was in AS BNR reactor

Figure 24 Zero air was forced flow in the chamber to clean the air inside it before the daily stocking gas would conducted

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Figure 25 Daily collecting gas was absorbed form the OSEGCC to the 10 L tedlar bag

Figure 26 The nitrous oxide emission sampling method in full scale wastewater treatment plant team

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3.3 Analytical procedures by GCMS

Gas samples from the OSEGCC were collected in 1 L tedlar bags (SKC, PA, USA) with a single polypropylene fitting. The bags contained a teflon syringe port lines septum and a hose connection that functioned as a shut off valve for incoming and outgoing gas. SKC air sampling pump (No. 224-PCXR8, PA, USA) was used to pump sample into the tedlar bag. Low flow 100 mL/min was applied and connected with midget impinge standard nozzle (SKC, PA, USA) in order to limit moisture from reactor. Gas samples (500 µL) were analyzed for nitrous oxide using Gas Chromatography with 5975C mass spectrometer (Agilent Technologies, 7890A). And column was a capillary with length 30 cm and dimensions of 0.320 mm (GC-Carbon plot).The detector, column, and injection temperature were 230, 110, 35°C respectively.

3.4 Zero Air10.5 Kg 150 Psi

Pure air composes of 78 % nitrogen 21 % oxygen and 1% of helium neon argon and xenon. Its weight is 10.5 Kg and pressure is 150 Psi, Zero air use to clean gases in the OSEGCC before we will start to collect. The small size can carry in the field.

3.5 Silica gel tube

Since we keep garb sample in the high moisture place such as the wastewater treatment plant. So the silica gel tube (3 cm diameter, 20 cm length) is design to connect with the OSEGCC to get rid of moisture before the sampling gas will absorbed to the tedlar bag.

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RESULT AND DISCUSSION

After the OSEGCC construction, it was tested leakage and tested transfer the chamber to the tedlar bag on the water surface before it would be floated on the real wastewater surface of the activated sludge (AS) with biological nitrogen removal (BNR) process in wastewater treatment plant Bangkok, Thailand.

1. Test Leak Result

A half an hour notice after light up aroma joss sticks caused white smoke inside the OSEGCC whether there was white smoke outside the chamber as shown in Figure 27. There is no white smoke leakage outside the chamber. So it is meant that the OSEGCC is no leakage. The other test method is pouring pure water into the acrylic glass chamber. But it might be broken because of the water weight.

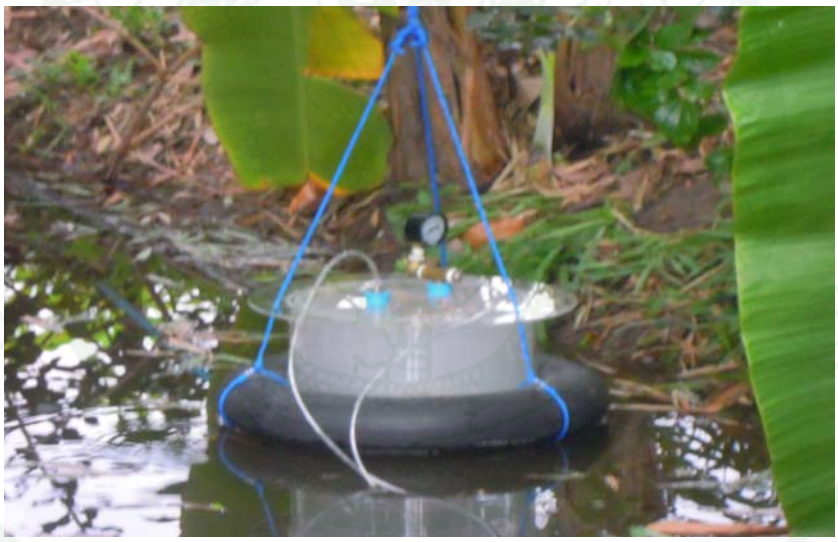

Figure 27 The white smoke was lighted up in the OSEGCC leakage test

2. Test Transfer Result

On the real experiment in wastewater treatment, the sampling gas must be absorbed through the very long 4.55 meter conduit. The pressure loss during flow through the long conduit causes the zero air pressure 150 psi was dropped, it would flow out the OSEGCC in to wastewater instead of flow along the conduit. Therefore the air absorbent pumps flow rate 500 ml/min need to absorb the zero air after press

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the zero air into the OSEGCC. However, if the more flow rate pump could be provided such as 1L/min, the sampling gas would be absorbed faster.

The transfer test was absorbing the white smoke from the OSEGCC through the 4.55 meter long conduit into the 10 L tedlar bag by the air absorbent pump. There was white smoke in the 10 L tedlar after 20 minutes absorbing. It is meant that the air absorbent pump could transfer the collecting gas to the OSEGCC as shown in Figure 28.

Figure 28 Test transfer the collecting gas from the OSEGCC to the 10 L tedlar bag by air absorbent pump

3. The Wastewater Treatment Influent

Physical and chemical characteristics of wastewater at the selected centralized wastewater treatment plant in Bangkok, which are from routine daily lab plant tests are given from the plant operator shown in Table 2 and 3.

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Table 2 Characteristics of influent in anoxic tank of AS BNR at the selected centralized treatment plant, Bangkok

Parameters	Anoxic Zone
NH_3^+(mg/L)	5.6
NO_2^- (mg/L)	0.08
NO_3^- (mg /L)	0.28
TKN (mg/L)	8.96
DO (mg/L)	0.85
COD (mg/L)	56.64
BOD (mg/L)	22.50
pH	6.81
Temp (°C)	29.0

Source : Drainage and Sewerage Department of Bangkok Metropolitan ,(2012).

Table 3 Characteristics of influent in aerobic tank of AS BNR at the selected centralized treatment plant, Bangkok

Parameters	TUE 20/09/11
NH_3^+ (mg /L)	7.56
NO_2^- (mg /L)	0.01
NO_3^- (mg /L)	0.33
TKN (mg /L)	14.56
DO (mg/L)	2.25
COD (mg/L)	95.20
BOD (mg/L)	33.75
pH	7.03
Temp(C)	29.0

Source : Drainage and Sewerage Department of Bangkok Metropolitan, (2012).

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3.1 Nitrous Oxide Measuring Results

After stocking sampling gas 24 hours as daily garb samples experimental design, it must absorbed to measure at the ERTC lab center ,Thailand. The garb samples of N_2O are measured by the GCMS Agilent Technologies 7890A at the ERTC, Thailand is shown in Table 4.

Table 4 Nitrous oxide emission result from anoxic zone and aerobic zone

N_2O concentration	Anoxic Zone	Aerobic Zone
(ppm)	25	17

Source : The Thailand ERTC Lab , (2012).

To find N_2O concentration from anoxic and aerobic zone of wastewater treatment, the headspace volume contained N_2O and the flux chamber volume sunk in wastewater contained NH_3-N, NO_2^-, NO_3^- and TKN should be calculated according to the dimension of the OSEGCC chamber dimension on Figure 29.

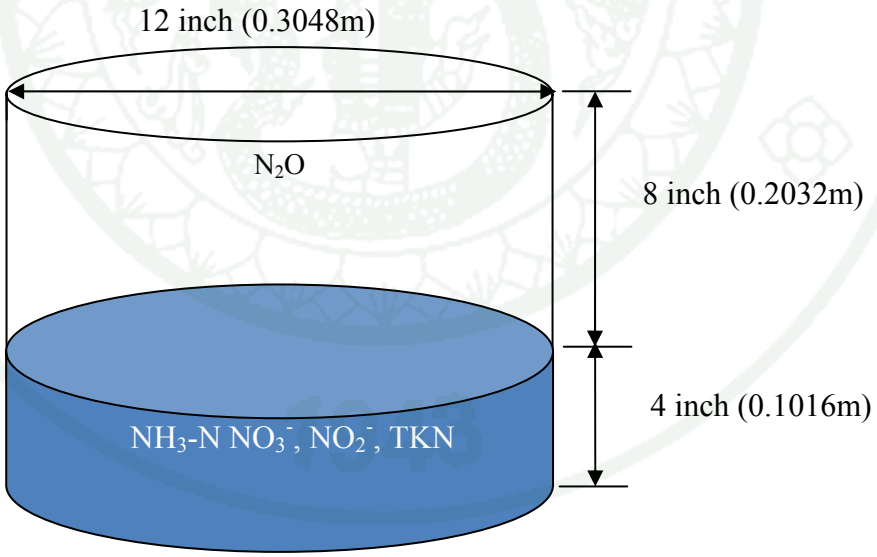

Figure 29 The onsite emission gas collecting chamber dimension

Volume of the OSEGCC $= \pi r^2 h$

$= (22/7)(6)^2(12)$

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Volume of the headspace = 14 L (0.014m^3)

Volume of the sank chamber = 7 L (0.007 m^3)

3.2 N_2O Concentration Calculated Assumption

In nitrous oxide concentration calculation, the detail data need to know such as the OSEGCC dimension, the BNR dimension, the wastewater flow rate and total number of populations release wastewater. The flux emission chamber from the wastewater surface in the OSEGCC area is the representative of the BNR area. Figure 30 is shown the assumption. Some factors could be illuminated such as nitrous oxide gas which was dissolved in WWTP below the OSEGCC should affect the overall concentration of nitrous oxide. In this work, the dissolved nitrous oxide gas below the OSEGCC would be neglected.

The wastewater treatment plant detail data were given from the selecting wastewater treatment plant administrator. The WWTP capacity is 350,000 m^3. The population in that area is 1,000,000 persons. The BNR dimension is 33 x 18 x 7 m^3. The wastewater flow rate is 100,000 m^3/d. The neglect dissolved N_2O and the OSEGCC and BNR dimension are shown in Figure 30.

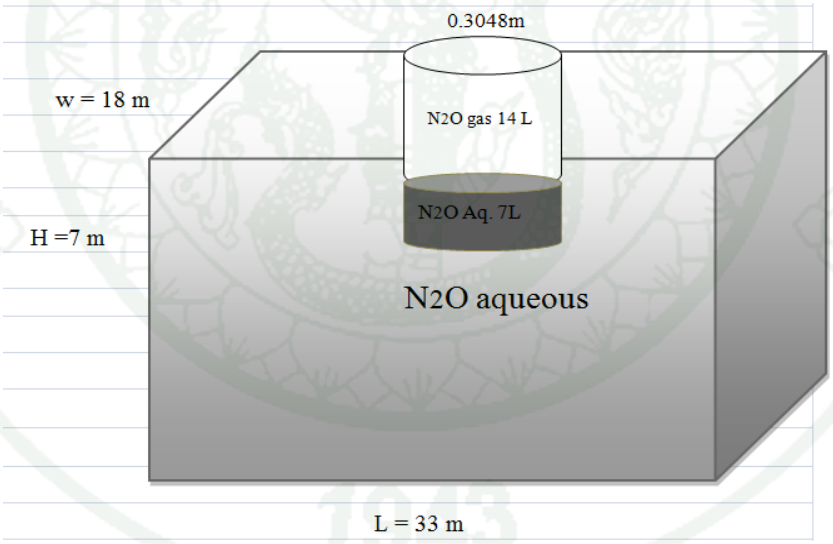

Figure 30 Shows status of nitrous oxide gas state and aqueous state in the OSEGCC which is floated in the 7 m deep BNR plant

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3.3 Law of Avogadro's

To convert ppm to a metric expression like $\mu g/m^3$, the density of gas can be calculated by the Law of Avogadro's, which says that equal volumes of gases, at the same temperature and pressure, contain the same number of molecules. This law implies that 1 mole of gas at STP a volume of 22.71 liters enfolds, also mentioned as the molar volume of ideal gas. Standard temperature and pressure (STP) is defined as a condition of 100.00 kPa (1 bar) and 273.15 K ($0^{\circ}C$). The amount of moles of the concerning gas could be calculated with the molecular weight.

From data details getting and neglect some parameters such as dissolved nitrous oxide, a little amount of NO_2^- 0.01 mg/L The N_2O flux area from the chamber was the representative of BNR flux area with the area ratio 8137.52 (Appendix C specimen calculation) Consequently, the nitrous oxide concentration calculated sequence both on an anoxic zone and an aerobic zone as shown in Appendix C Specimen calculation. The final results in % nitrogen load and g N/ person/yr are shown in Table 5 and 6.

Table 5 The nitrous oxide calculated results corresponding to % N load

Unit	Anoxic zone	Aerobic zone
ppm	25	17
% N load	0.44	0.35

Table 6 The nitrous oxide calculated results corresponding to % g N/person/yr

Unit	Anoxic zone	Aerobic zone
ppm	25	17
g N/person/yr	0.00114	0.00079

Discussion

1. Compare Results with The IPCC Limits

Accord to the IPCC in 2006 specifics that for countries with advanced centralized WWTPs, the direct emission from WWTPs is 3.2 g N/person/year, corresponding to approximately 0.035% N_2O emission of the nitrogen load of a WWTP.

Compare the IPCC N_2O emission limit form WWTP with the measuring N_2O results transform in g N/person/year unit and % N load in both in anoxic zone and in aerobic zone also shown in Table 5 and 6.

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The nitrous oxide emission concentration in ppm from the selected WWTP when it transfer to 0.44 and 0.35 % N load of the influent. The calculation method is shown in Appendix C. Its emission is over the limit of the IPCC. That is because of the NH_3-N in the influent is very low. As review in the literature that parameter leading to its emission such as low COD/N ratio. In this research, the COD/N ratio is about 10 which is quite low. So its emission is high (25 ppm, 17 ppm). Therefore when we compare % N form nitrous oxide emission with % N from the NH_3-N. The % N ratios are high 0.44 % and 0.35 % respectively. However, the results are relevant to the low COD/N ratio leading to high nitrous oxide emission both in nitrification (0.35 %) and detrification (0.44%) process. The emission is over the IPCC limit (0.035 %)

The nitrous oxide emission concentration in ppm from the selected centralized WWTP when it is transfer to 0.00114 and 0.00079 g N/person/yr in anoxic zone and in aerobic zone respectively. The calculation method is shown in Appendix C (Specimen Calculation). The nitrous oxide calculated results corresponding to % g N/person/ yr are shown in Table 6. Compare with the IPCC limit, it is less than the 3.2 g N/person/yr**.** In this case the total population in that area is 1,000,000 persons. Therefore the emission per head is very less than the IPCC limit.

2. Nitrous Oxide Emission from Nitrification and Denitrification

In this work, the nitrous oxide concentration in anoxic zone is expected to find most because it is rarely oxygen as the review literature. The sampling measurement in anoxic zone is 25 ppm more than in aerobic zone which is 17 ppm as expectation. Compare with the nitrous oxide sampling in 1,000 million gallon wastewater treatment plant (bigger than the selected plant in this research 8,500 times). The nitrous oxide sampling result was shown 22 ppm in aerobic zone and 1.5 ppm in anoxic zone (Chandran, 2009). That result implies that the aerobic zone may be the nitrous oxide major source. However, it cannot still certainly unidentified that nitrification process or dinitrification process is truly the nitrous oxide main source at present.

However, the experiments have been done only 2 rounds in anoxic zone and anaerobic zone in one wastewater treatment plant. So it could not conclude nitrous oxide major source or parameters leading. But the experiment results show that there are truly nitrous oxide emission from full scale wastewater treatment plant with high amount because the developed onsite emission gas collecting chamber can keep the sampling gas with correct method or follow the USEPA method (Protocol U4R07 which was approved by USEPA).

The more experiments should use the OSEGCC sampling gas in any municipal wastewater treatment plants to survey the nitrous oxide emissions and make its record to study its emission causes.

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3. The Onsite Emission Gas Collecting Chamber Development Result

Collecting gas by the OSEGCC is very well. The cost is one tenth with compare with the SEIFC (exclude shipping). Simple idea of develop the OSEGCC is construct the close flux chamber floating on the wastewater surface. In practical, sampling gas is absorb to a tedlar bag and then send to the lab for measuring in Thailand. Thus the sampling gases are not real emission concentration. It is less than its real emission. The gas emission is gone away. So it should be covered by the close flux chamber. And the material or cleaning gas should select the opposite matter with the sampling gas. For example, in this work, sampling gas is nitrous oxide which is inorganic gas, the acrylic glass which is use to compose the OSEGCC because it is organic matter. The 4.55 meter teplon conduits, which were organic material, were also chosen. Cleaning gas inside the chamber was used zero air because of its cost. It should actually use helium gas as specific in protocol U4R07 because it is inert gas and no reaction with nitrous oxide but it is too expensive. Therefore, the zero air was selected. When the nitrification and denitrification process occur by bacteria with oxygen and without oxygen, many kinds of gases are emitted such as N_2 NO NO_2 N_2O. The pressure inside the OSEGCC at the beginning is 1 ATM was increase. If gas emission factor and flux are wanted to find, the rotameter port should provided to find the increasing pressure. The pressure gauge was not sensitive enough to measure it. However, the developed OSEGCC was very well inventions because it could be keep the high gas concentration and it was made in Thailand. It could be the model for commercial environmental sampling gas product.

4. The Analytical Instrument

The gas chromatography with 5975C mass spectrometer (Agilent Technologies, 7890A) could be measured nitrous oxide in this research because the sampling nitrous oxide concentration is quite high in ppm. However if its concentration is less in ppb, the GC detect type ECD should be provided. The standard gas which used in measurement is important. It is expensive and must also be imported. So the sampling gas concentration has to estimate that it is in ppb or ppm. If the sampling gas concentration is in ppb whereas the gas standard is in ppm, it could not measure because it is different scale. However, the ppm standard gas could be diluted to ppb concentration but the original concentration standard gas could used to compare better.

In the literature review, the analytical instrument such as the TELEDYNE model 320E is used to measure online monitoring. However, it is hard to find in Thailand. This analytical instrument could be measured all nitrogen green house gases. If the carbon credit trade market is more popular in Thailand than at present. This analytical measurement could be provided easier.

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CONCLUSION AND RECOMMENDATION

Conclusion

The nitrous oxide gas emission sampling method during biological nitrogen removal on the full scale activated sludge municipal wastewater treatment plant in Bangkok Thailand was the first time measuring experiment in Thailand. The preparing schedule plan has begun since year 2009. It was starting with contacting the honest person who was the Paul L.Busch Award winner has devised a novel technology to turn the methane in biogas into methanol form WERF. The author found him from YouTube. He kindly sent the protocol U4R07 (Characterization of Nitrogen Greenhouse Gas Emission from Wastewater Treatment BNR Operations), which was approved by the USEPA as it was review in the previous literature.

So the developed onsite collecting gas chamber was the replica from the surface emission isolating flux chamber which was accepted by USEPA which was concerned that it would be used in the AS BNR completely mixed reactor of the selected cauterized wastewater treatment in Thailand.

Moreover, the sampling method was acted under the protocol U4R07 is studied deeply, sometimes consulted with Professor Dr. Kartik Chandran through the email and the mobile phone to apply the nitrous oxide gas online monitoring to be keeping garb samples since the limit of the analytical instrument such as teledyne or GCMS to work in the WWTP field. Due to the WWTP operation business might be effected cause of green house gases emission. Therefore, in this work, there were only two times garb samples. However, nitrous oxide emissions were found in ppm both in aerobic and anoxic zones.

The developed OSEGCC and the protocol U4R07 could be applied for nitrous oxide sampling method for full scale WWTP significantly. However, more studies and samples could be needed in order to identify the main cause of nitrous oxide gas from WWTP. Moreover, the nitrous oxide gas emission from WWPT is 26 % of green house effect gas from water chain so it is significantly important to reduce nitrous oxide emission. The results of N_2O productions from WWTP with BNR from this work could be used as a guideline for survey N_2O emission from WWTP in the future.

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Recommendation

In the future work, The further researches could measure all the characterize of nitrogen gases measurement all WWTPs of Municipal Thailand by this developed OSEGCC and the protocol U4R07 with on line monitoring (The GCMS or the Teledyne analytical instrument is need to place on line monitoring in the flied work) The results could be used to improve the operation of WWTPs to minimize green house gases.

Since green house gases measuring could damage the WWTP business which mostly operated by the company contracted with the municipal. Therefore, it would quite be hard to work this research of GHG in WWTP. The action should have permission from authorize organization such as public health ministry. And the experiment research could be done follow this research because it was done under the protocol U4R07 approved by USEPA. Moreover, the online monitoring will be shown characterize of nitrogen gases such as NO, NO_2, N_2O and also the GCMS or the Teledyne Monitor 320 E analytical instrument should be provided in the field work.

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APPENDICES

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Appendix A
Table

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Appendix Table A1 Effluent Data in from the selecting WWT plants Bangkok Thailand

	MON 19/09/11	TUE 20/09/11	WED 21/09/11
Effluent	mg/L		
NH3-N	0.11	0.11	0.11
NO2-	0.03	0.03	0.03
NO3-	4.55	4.70	4.65
TKN	1.12	1.40	2.80
DO	7.10	6.30	6.20
COD	18.88	26.66	19.20
BOD	4.65	6.60	4.20
PH	6.42	7.02	6.82
Temp (C)	29.0	29.0	30.0

Source : Drainage Department and Sewerage of Municipal Thailand, 2012.

Appendix Table A2 Measuring Results of Nitrous Oxide by GCMS

	MON 19/09/11 (anoxic zone)	TUE 20/09/11 (aerobic zone)
	(ppm)	
N_2O	25	17

Source : Drainage Department and Sewerage of Municipal Thailand, 2012.

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Appendix B
Figure

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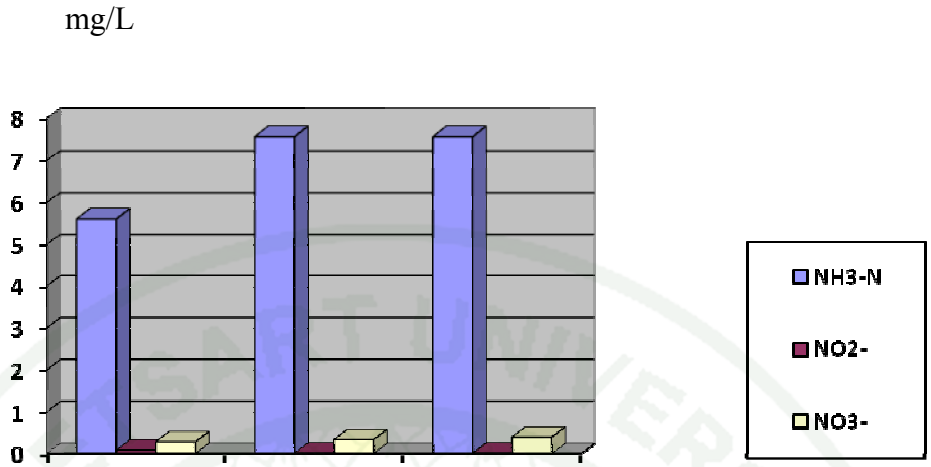
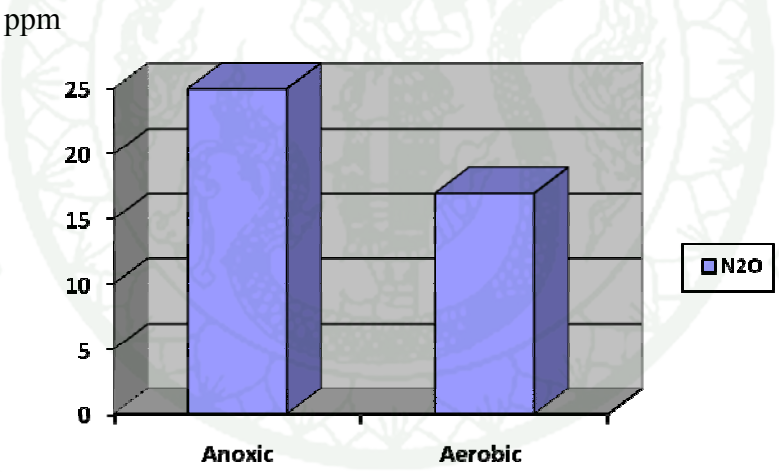


Appendix Figure B1 Nitrogen Influent from the selected wastewater treatment plant



Appendix Figure B2 Daily nitrous oxide emission in aerobic zone and anoxic zone

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Appendix C
Specimen Calculation

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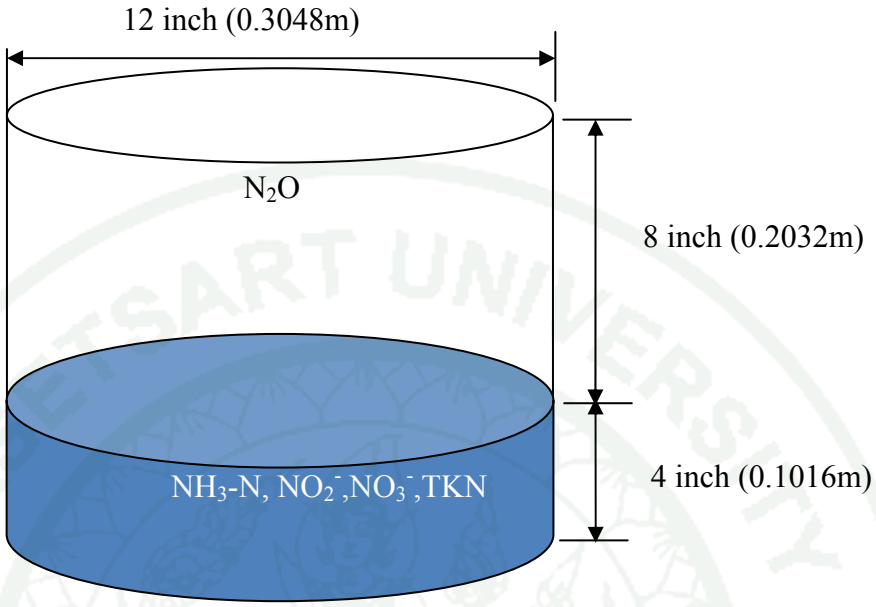
Calculation of Nitrous Oxide Emission from ppm to mg/L ,% N Load and g N/person/yr



Appendix Figure C3 The onsite emission gas collecting chamber dimension

To find N_2O concentration from anoxic zone of wastewater treatment plant

Volume of the chamber = $\pi r^2 h$
= $(22/7)(6)^2(12)$
= 21 L

Volume of the headspace = 14 L (0.014 m^3)

Volume of the chamber in wastewater = 7 L (0.007 m^3)

Find N_2O mole in gaseous stage = 25 ppm
= 25 µl/L

It implies that there is N_2O 25 µl in Air 1 L. Or 1,000,000 L air there is N_2O 25 L

Assumption

1. Since the deep of BNR plant is deep 7 m. But the chamber collects gas only wastewater surface. Nitrous oxide which dissolves below the OSEGCC should affected the overall concentration of nitrous oxide. But we will neglect its concentration.

2. The WWTP Capacity = 350,000 m3 , the BNR dimension = 33 x 18 x 7 m3

3. The wastewater flow rate is 100,000 m3/d

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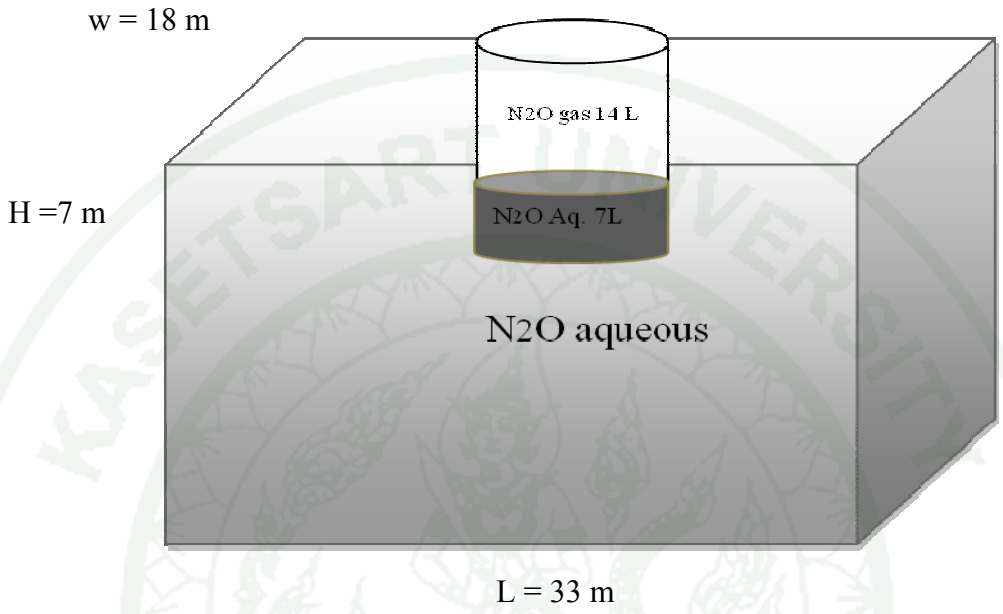

Appendix Figure C4 Shows status of nitrous oxide gas state and aqueous state in the OSEGCC which is floated in the 7 m deep BNR plant

To convert ppm to a metric expression like µg/m^3. The density of gas can be calculated by the Law of Avogadro's, which says: equal volumes of gases, at the same temperature and pressure, contain the same number of molecules. This law implies that 1 mole of gas at STP a volume of 22.71108 liters enfolds, also mentioned as the molar volume of ideal gas. Standard Temperature and Pressure (STP) is defined as a condition of 100.00 kPa (1 bar) and 273.15 K (0°C), The amount of moles of the concerning gas can be calculated with the molecular weight.

In aerobic zone, the 25 µl/L nitrous oxide was kept at 29°C temperatures, a little different pressure change from 1atm pressure. To convert to concentration to mg/L

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

Where P_1, P_2 is 1 ATM

T_1 is 29 ° C or 302° K

T_2 is 0 ° C or 273 ° K

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V_1	=	25μL	
V_2	=	25 μL*273 º K/302 º K	
	=	0.00002260	L
P_2V_2	=	n_2RT	

Where P_2 = 1atm V_2= 2.2599 x$10^{\wedge -5}$ L ,R = 0.082057 L. atm-$k^{\wedge -1}$- $mole^{\wedge -1}$

n_2	=	0.00000101	mole
Since N_2O molecular weight	=	44	g
So the N_2O emits in weight	=	0.00004442	g/L

But the OSEGCC volume

The 14 L nitrous oxide emission	=	0.00062188	g
The overall surface of the WWTP	=	(33m*18m)	
	=	549 m^2	
The OSEGCC : BNR Reactor Surface ratio	=	8137.52	
The N_2O emission per day	=	(0.00062188 g) / (8137.516275)	
	=	5.060558621	g
The N_2O emission per year	=	1801.56	g/yr
In this area there are 1,000,000 Persons	=	0.001146447	g-N/person-yr

To find nitrous oxide emission corresponding to % N Load / a WWT plant

Total N_2O emission from BNR	=	5.060558621	g/d
	=	3.220355486	g/d
$N\text{-}N_2O$	=	2.049317128	g/d

In Anoxic Operation Total NH_3-N Influent = 5.6 mg/L NO_2^- and NO_3^- are neglect because its concentration is low

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	=	5,600	$mg/m^3/d$
mass flow rate of wastewater	=	100,000	m^3/d
Volume of NH_3-N	=	560,000	g/d
Mole regular weight of NH_3-N	=	17	g
	=	560000 *(14/17)/1000g	
	=	461.1764706	g
N_20 emission	=	0.004444	
	=	**0.44% N Load**	

In aerobic zone The 17 µl/L nitrous oxide was kept at 29°C temperatures, a little different form 1atm pressure. To convert its concentration to mg/L

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

T_2 is 0 ºC or 273 º K

V_1 = 17µL

Therefore V_2 = 17 µL*273 º K/302 º K

= 15.36754967 µ L

= 0.000015 L

P_2V_2 = n_2RT

Where P_2 = 1atm V_2= 1.536 x10^{-5} L R = 0.0 82 L.atm-k^{-1}- $mole^{-1}$

n_2 = 0.00000069 mole

Since N_2O molecular weight	=	44	g
So the N_2O emits in weight	=	0.00003021	g
But the OSEGCC volume	=	0.00003021*14	g
The 14 L nitrous oxide emission	=	0.000422872	g
The overall surface of the WWTP	=	(33m*18m)	

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	=	549	m^2
the OSEGCC : BNR Reactor surface ratio	=	8137.52	
The N_2O emission per day	=	3.44	g
The N_2O emission per year	=	1256.01	g/y

To find nitrous oxide emission corresponding to % N Load / a WWT plant

The N_2O emission per day	=	3.44113864	g
The N- N_2O emission per day	=	2.189815498	g

In aerobic operation

Total NH_3-N Influent	=	7.56	mg/L

(NO_2^- and NO_3^- are neglect because its concentration is low)

Mole regular weight of NH_3-N	=	17 g	
N-NH_3	=	0.00756 *(14/17)	
	=	6.225882353	mg/L
	=	0.006225882	g/L
Mass flow rate of wastewater	=	100000.00	m^3/d
mass N-NH_3	=	622.58	g/d
Nitrous oxide emission	=	0.003517	
	=	**0.35 % N load**	

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Appendix D
Photograph

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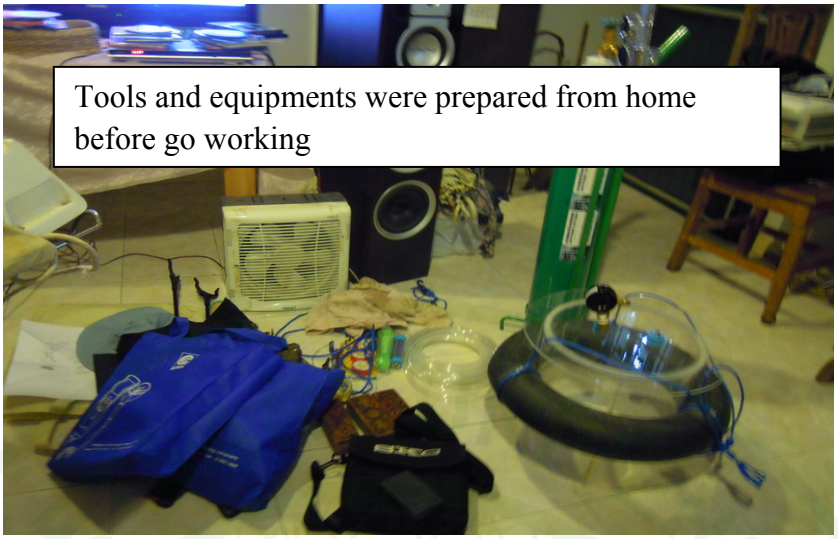
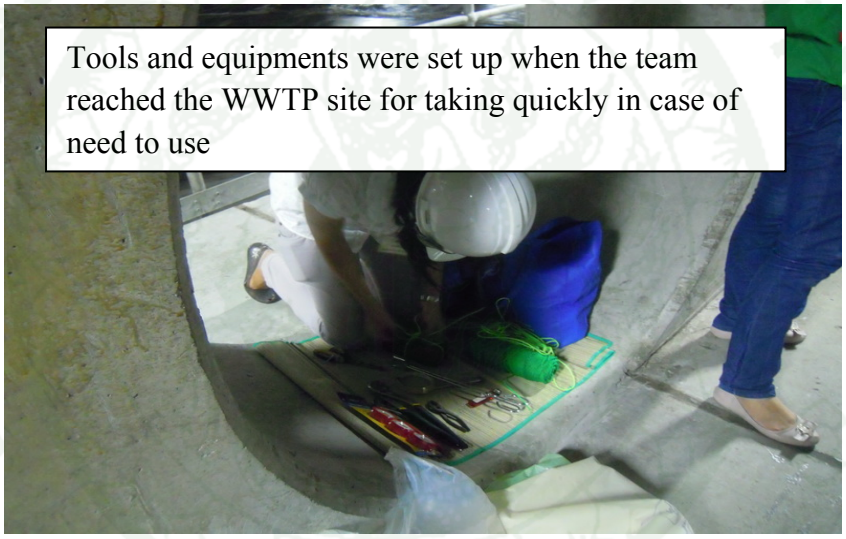


Tools and equipments were prepared from home before go working



Tools and equipments were set up when the team reached the WWTP site for taking quickly in case of need to use

The OSEGCC in an anoxic zone

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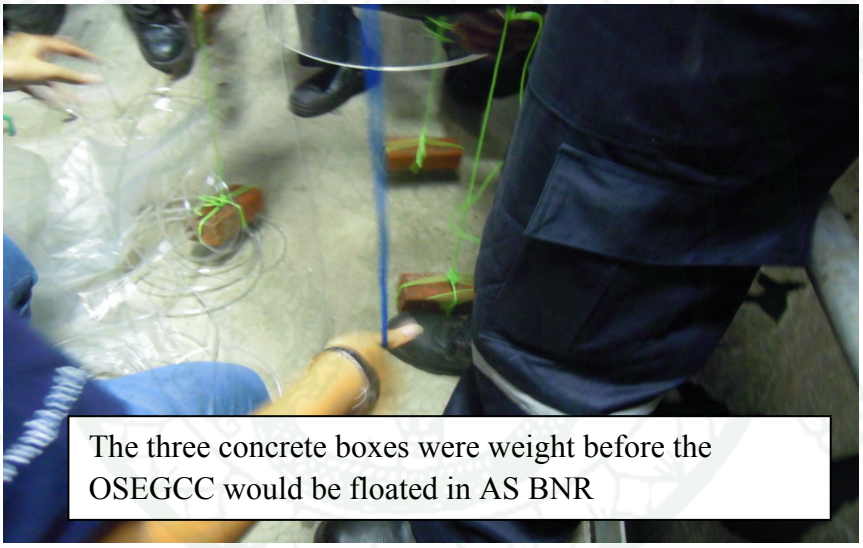
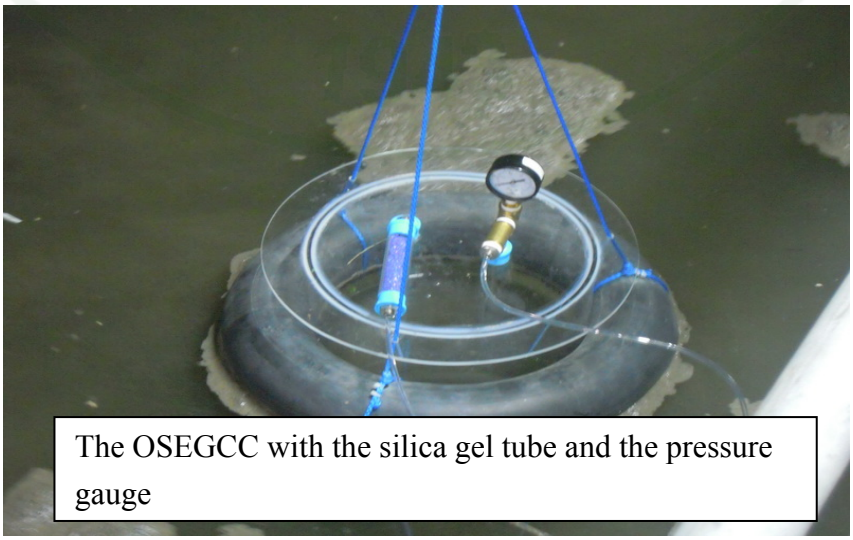
Zero air was absorbed to the teldar bag after cleaning the OSEGCC



The three concrete boxes were weight before the OSEGCC would be floated in AS BNR



The OSEGCC with the silica gel tube and the pressure gauge

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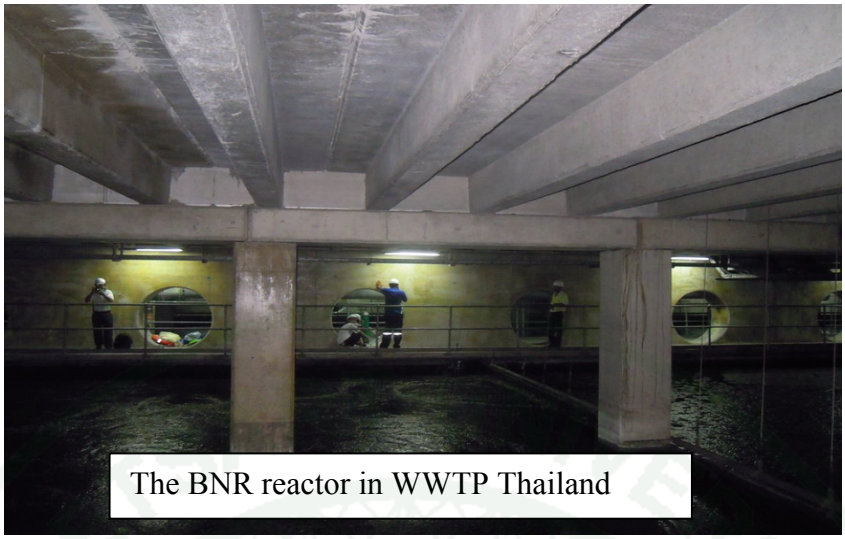
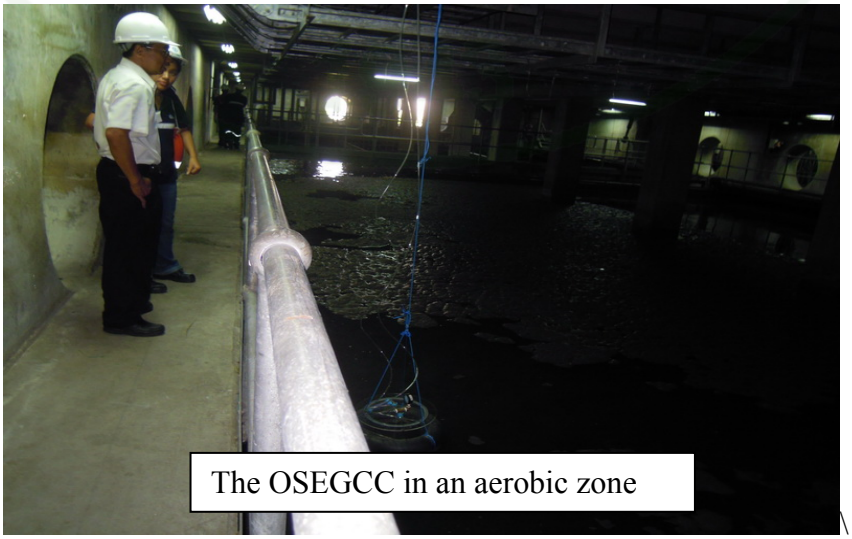


The BNR reactor in WWTP Thailand

The OSEGCC in an aerobic zone



The OSEGCC in an aerobic zone

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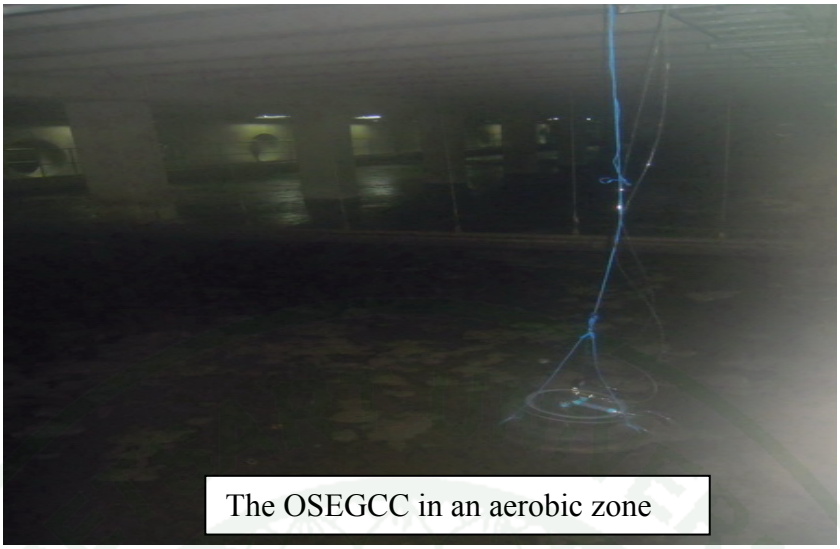

The OSEGCC in an aerobic zone

The Zero air was taken home

The OSEGCC was cleaned after finish

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The OSEGCC team

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CURRICULUM VITAE

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