Activated sludge: 100 *plus* 1 years - New trends and perspectives

Greenhouse gases production in wastewater treatment plants

Donatella CANIANI, University of Basilicata

Marianna CAIVANO, University of Basilicata

Ministero dell'Istruzione Università e Ricerca

PRIN 2012

Outline

1. THE ISSUE
2. GHG emissions from WWTPs
3. GHG modeling
4. FIELD MEASUREMENTS
5. LITERATURE ANALYSIS: Strengths & Weaknesses
6. FUTURE DEVELOPMENTS

2. LITERATURE REVIEW. GHG EMISSIONS FROM WWTPs.

Conventional activated sludge WWTPs are the most widely used

TREATMENT UNITS

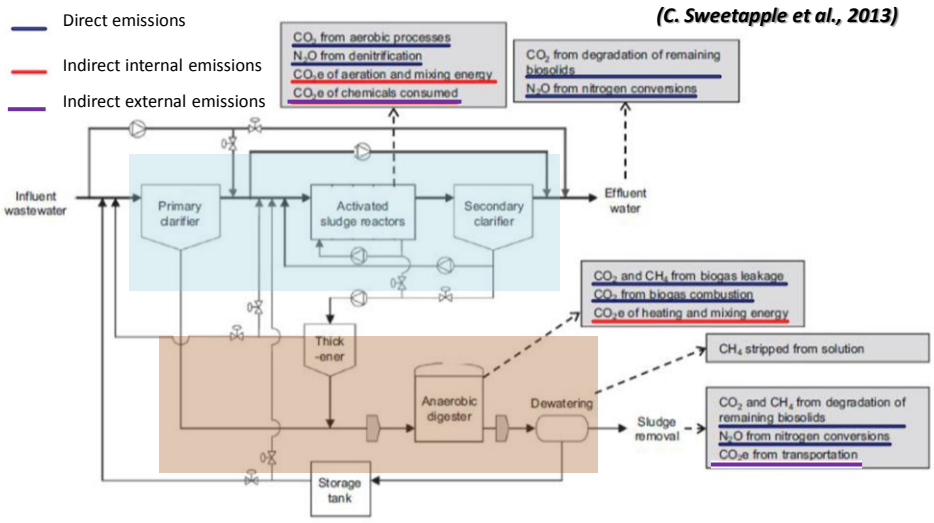
1. Equalization
2. Screening
3. Aerated grit chamber
4. Primary clarifier
5. Activated sludge tank
6. Secondary clarifier
7. Filtration
8. Disinfection
9. Thickening
10. Anaerobic digestion tank
11. Dewatering
12. Offices

WWTP of Potenza (Basilicata, Italy)

2. LITERATURE REVIEW. GHG EMISSIONS FROM WWTPs.

Direct emissions VS Indirect emissions

Schematic diagram of the modified BSM2 plant and sources of modelled GHG emissions.
(C. Sweetapple et al., 2013)



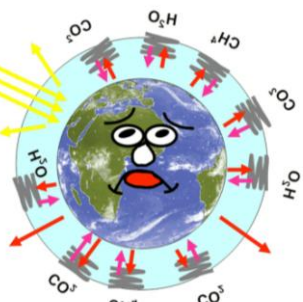
1. THE ISSUE.

What is the issue?

CH_4

CO_2

N_2O



Senza effetto serra naturale:
T media terrestre ≅ -25 °C

Con effetto serra naturale:
T media terrestre ≅ 15 °C

Con effetto serra rafforzato in modo artificiale:
T media terrestre ≅ ??? °C

GREENHOUSE GASES

2012 PRIN

GWP (Global Warming Potential)

Carbon dioxide(CO_2) = 1

Methane (CH_4) = 24

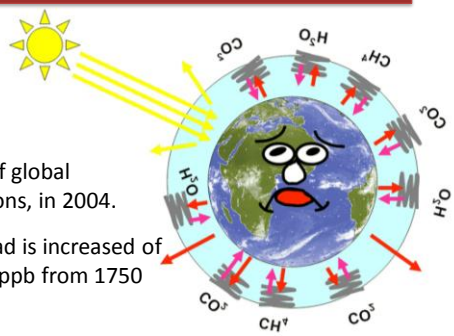
Nitrous oxide (N_2O) = 310

ipcc INTERGOVERNMENTAL PANEL ON climate change

1. THE ISSUE.

What is nitrous oxide?

N_2O



Senza effetto serra naturale:
T media terrestre ≅ -25 °C

Con effetto serra naturale:
T media terrestre ≅ 15 °C

Con effetto serra rafforzato in modo artificiale:
T media terrestre ≅ ??? °C

- It represents the 7.9 % of global anthropogenic GHG emissions, in 2004.
- The N_2O atmospheric load is increased of 16 %, from 270 ppb to 319 ppb from 1750 to 2005
- The emission of N_2O from water utility represents the 3% of global emissions from every source and it is the sixth most important contribution; It will increase by 13% from 2005 to 2020.

ipcc INTERGOVERNMENTAL PANEL ON climate change

The production of N_2O in WWTPs is still unclear

2. LITERATURE REVIEW. PROCESSES FOR GAS PRODUCTION.

Direct and indirect internal EMISSIONS

- ORGANIC MATTER OXIDATION IN AEROBIC CONDITION (biomass respiration)
- NITRIFICATION
- DENITRIFICATION
- NITRIFIER DENITRIFICATION
- ORGANIC MATTER OXIDATION IN ANAEROBIC CONDITION
- ENERGY CONSUMPTION

LITERATURE RANGE:
0.5 – 2 kg_{CO2e} / mc_{ww}

INDIRECT external EMISSIONS

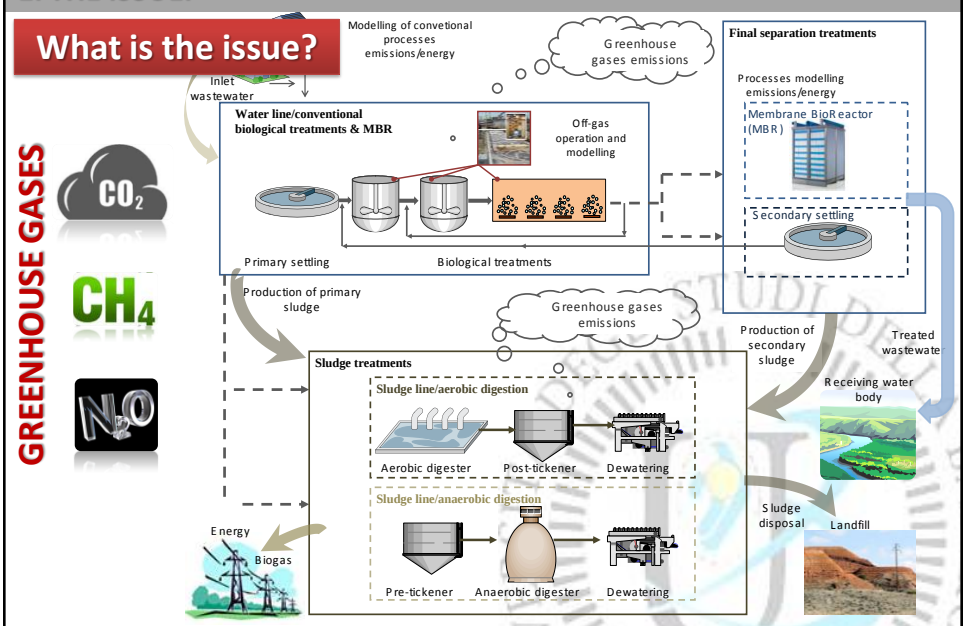
- CHEMICALS PRODUCTION AND TRANSPORTATION
- SLUDGE TRANSPORTATION, DISPOSAL OR REUSE

N_2O production from biological processes is still unclear

LITERATURE RANGE:
0.017 – 80 mg_{N2O}/l
SATURATION CONCENTRATION:
0.53 mg_{N2O}/l

1. THE ISSUE.

What is the issue?



2. LITERATURE REVIEW. PROCESSES FOR GAS PRODUCTION: Nitrogen Removal

NITRIFICATION | **DENITRIFICATION**

Nitrification in the oxidation of dell'NH_4^+ to NO_3^- via NO_2^-, as represented by following reactions:

$$NH_4^+ + 3/2\ O_2 \longrightarrow NO_2^- + 2H^+ + H_2O$$

$$NO_2^- + ½\ O_2 \longrightarrow NO_3^-$$

IT IS PERFORMED BY THIS BACTERIA

Nitrosomonas	Primary nitrifiers or ammonium – oxidizing bactiera **(AOB)** that oxidize the NH_4^+ to NO_2^-
Nitrobacter	Secondary nitrifiers or nitrite – oxidizing bacteria **(NOB)** that oxidize the NO_2^- to NO_3^-

Autotrophic aerobic bacteria.
The organic carbon is their only carbon source.
The energy for their growth is taken from reactions.

REACTION ENVIRONMENT
Aerobic

2. LITERATURE REVIEW. PROCESSES FOR GAS PRODUCTION: Nitrogen Removal

NITRIFICATION | **DENITRIFICATION**

The denitrification is the stepwise reduction of NO_3^- to N_2, as represented by the following reaction:

$$C_{10}H_{19}O_3N + 10\ NO_3^- \longrightarrow 5N_2 + 10CO_2 + 3H_2O + NH_3 + 10OH^-$$

IT IS PERFORMED BY THIS BACTERIA

Pseudomonas

Heterotrophic facultative bacteria.
The organic carbon is used for both anabolic and catabolic pathways.
The NO_3^- is used in place of oxigen as an electron acceptor in anoxic conditions.

REACTION ENVIRONMENT
Anoxic

2. LITERATURE REVIEW. PROCESSES FOR GAS PRODUCTION: Nitrogen Removal

NITRIFICATION | **DENITRIFICATION**

$NH_4^+ + 3/2\ O_2 \xrightarrow{Nitrosomonas} NO_2^- + 2H^+ + H_2O$

$NO_2^- + ½\ O_2 \xrightarrow{Nitrobacter} NO_3^-$

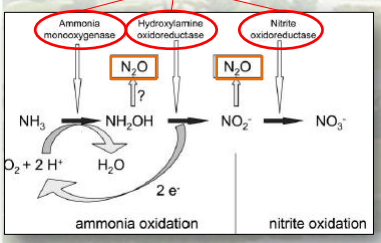
Intermediate reactions

$NH_4^+ + ½\ O_2 \longrightarrow NH_2OH + H^+$

$NH_2OH + O_2 \longrightarrow NO_2^- + 2H^+ + H_2O$

Intermediate: NH_2OH HYDROXYLAMINE

ENZYMES CATALYSING



Outline of the pathway and enzymes involved. *(N. Wrage et al., 2001)*

N_2O is formed during the chemical decomposition of intermediates, such as hydroxylamine and nitrite.

N_2O is also produced during the incomplete oxidation of NH_2OH because of formation of nitrosyl radical (NOH).

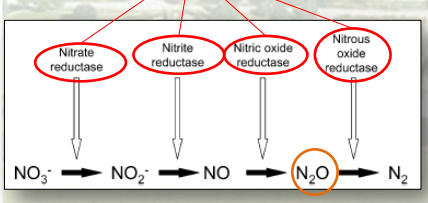
2. LITERATURE REVIEW. PROCESSES FOR GAS PRODUCTION: Nitrogen Removal

NITRIFICATION | **DENITRIFICATION**

$C_{10}H_{19}O_3N + 10\ NO_3^- \xrightarrow{Pseudomonas} 5N_2 + 10CO_2 + 3H_2O + NH_3 + 10OH^-$

The denitrification pathway is a sequence of biochemical reactions :

ENZYMES CATALYSING



Outline of the denitrification pathway and enzymes involved. *(N. Wrage et al., 2001)*

N_2O is an intermediate in the denitrification pathway. It is not a product of chemical rection!

2. LITERATURE REVIEW. PROCESSES FOR GAS PRODUCTION: Nitrogen Removal

HETEROTROPHIC NITRIFICATION | **NITRIFIER DENITRIFICATION**

Some heterotrophic bacteria can also nitrify. The organic carbon is used for both anabolic and catabolic pathways. Intermediates and chemical products of heterotrophic and autotrophic nitrification are the same, the enzymes of the two processes have been shown to differ from each other. They produce NO_3^- during organic nitrogen oxidation under aerobic condition.

N_2O is produced (as with denitrification) as an intermediate of reactions. Under aerobic conditions, heterotrophic nitrifiers produce much more N_2O per cell than autotrophic nitrifiers . (N. Wrange et al., 2001).

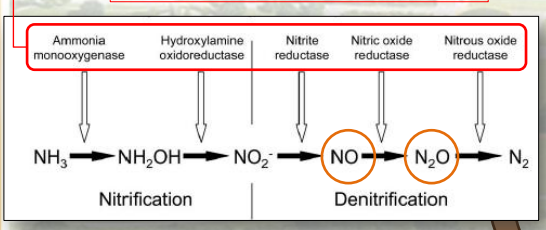
2. LITERATURE REVIEW. PROCESSES FOR GAS PRODUCTION: Nitrogen Removal

HETEROTROPHIC NITRIFICATION | **NITRIFIER DENITRIFICATION**

More than 35 years ago, it was proposed that same nitrifiers could not only nitrify, but denitrify as well; this pathway of nitrification, called **nitrifier denitrification**, might contribute to a major part of the loss of ammonium in the form of NO ed N_2O.

It is a pathway in which the oxidation of NH_3 to NO_2^- is followed by the reduction of NO_2^- to N_2O and N_2, **without NO_3^- production**.

PROBABLE ENZYMES CATALYSING



Nitrifier denitrification: hypotetical pathway and probable enzymes. *(N. Wrage et al., 2001)*

This sequence of rections in perfermed by **autotrophic ammonium – oxidizing bacteria**; ***Nitrosomonas europaea*** is the best studied.

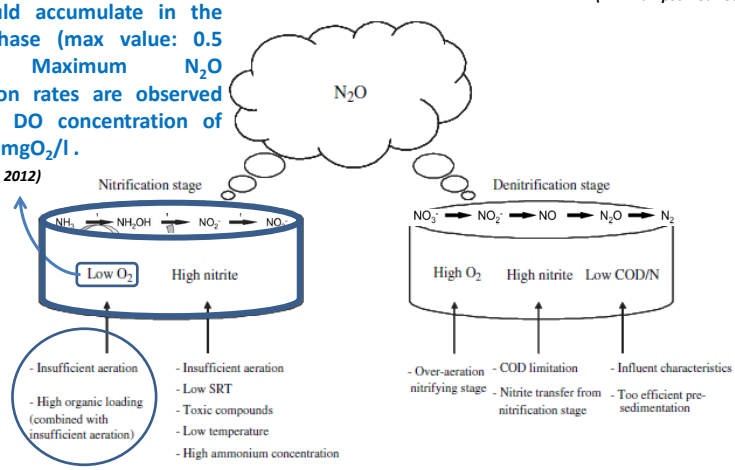
2. LITERATURE REVIEW. FACTORS INFLUENCING N_2O EMISSIONS.

Aeration rate and DO concentration | Nitrite concentration | Organic carbon concentration | Availability of copper ions

INCOMPLETE NITRIFICATION: N_2O could accumulate in the liquid phase (max value: 0.5 mg/l). Maximum N_2O production rates are observed between DO concentration of 0.1 – 0.3 mgO_2/l .

(Y. Law et al. 2012)

Main parameters leading to N_2O emissions.
(M.J. Kampschreur et al., 2009)



LOW AERATION RATE

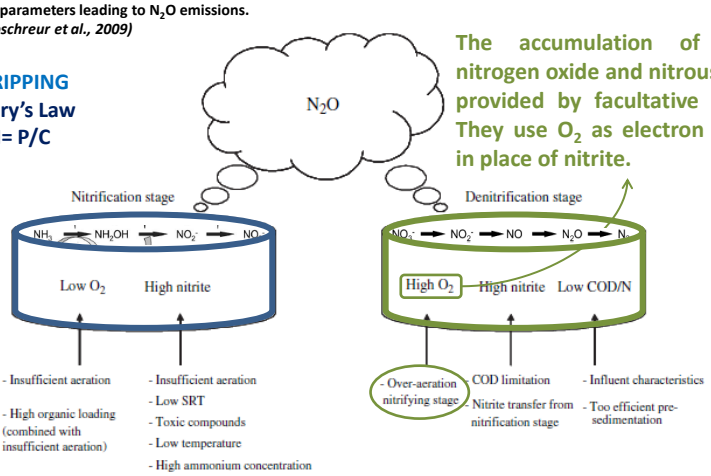
2. LITERATURE REVIEW. FACTORS INFLUENCING N_2O EMISSIONS.

Aeration rate and DO concentration | Nitrite concentration | Organic carbon concentration | Availability of copper ions

Main parameters leading to N_2O emissions.
(M.J. Kampschreur et al., 2009)

STRIPPING
Henry's Law
H= P/C

The accumulation of nitrate, nitrogen oxide and nitrous oxide is provided by facultative bacteria. They use O_2 as electron acceptor in place of nitrite.

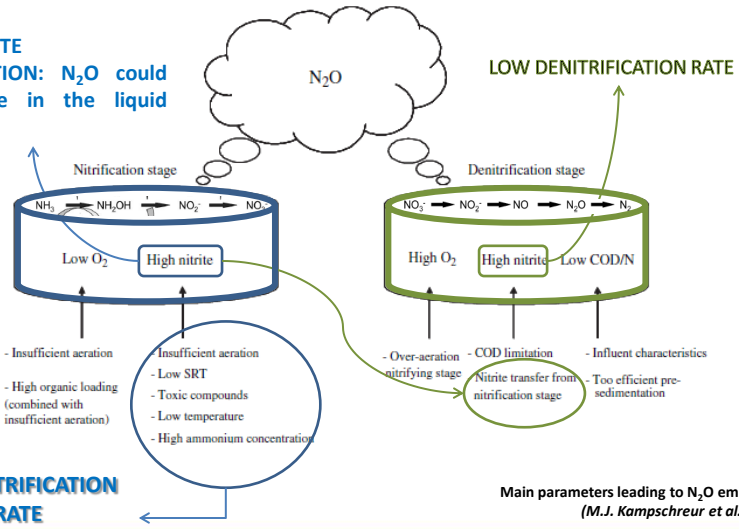


HIGH AERATION RATE

2. LITERATURE REVIEW. FACTORS INFLUENCING N_2O EMISSIONS.

Aeration rate and DO concentration | **Nitrite concentration** | Organic carbon concentration | Availability of copper ions

INCOMPLETE NITRIFICATION: N_2O could accumulate in the liquid phase .



LOW NITRIFICATION RATE

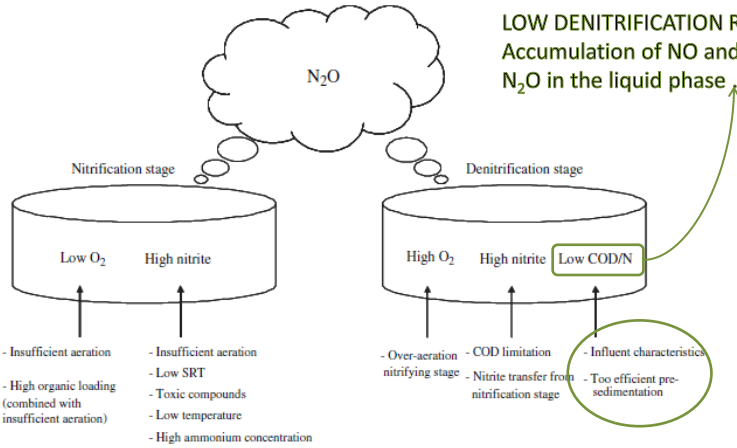
Main parameters leading to N_2O emissions.
(M.J. Kampschreur et al., 2009)

2. LITERATURE REVIEW. FACTORS INFLUENCING N_2O EMISSIONS.

Aeration rate and DO concentration | Nitrite concentration | **Organic carbon concentration** | Availability of copper ions

Main parameters leading to N_2O emissions.
(M.J. Kampschreur et al., 2009)

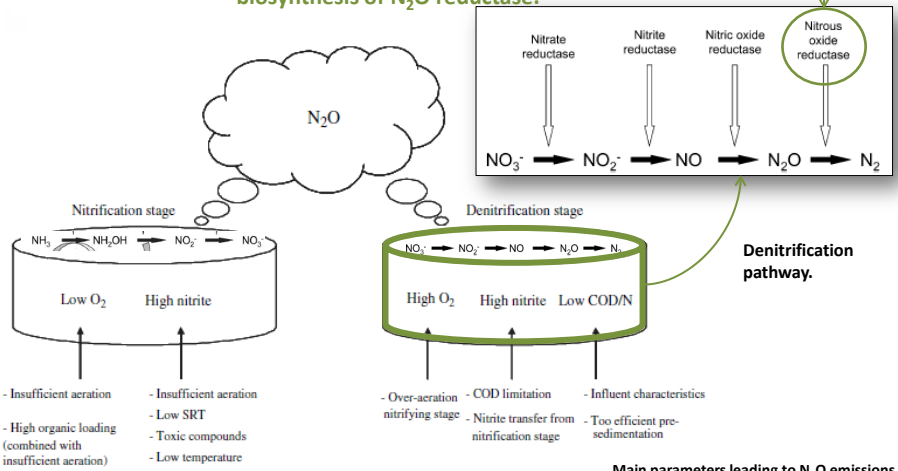
LOW DENITRIFICATION RATE: Accumulation of NO and N_2O in the liquid phase



2. LITERATURE REVIEW. FACTORS INFLUENCING N_2O EMISSIONS.

Aeration rate and DO concentration | Nitrite concentration | Organic carbon concentration | Availability of copper ions

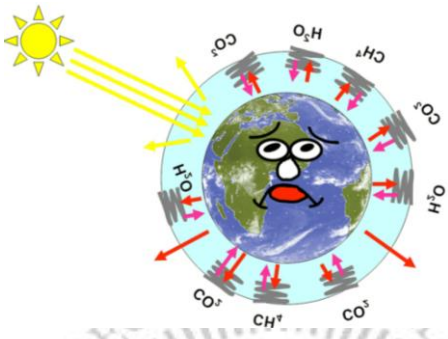
Copper ions are essential in biosynthesis of N_2O reductase.



Main parameters leading to N_2O emissions. *(M.J. Kampschreur et al., 2009)*

FACTORS INFLUENCING N_2O PRODUCTION AND EMISSION.

POSSIBLE MITIGATION STRATEGIES



Minimizing the production in the liquid phase:

- ❑ Ensure a longer sludge retention time.
- ❑ Ensure a dissolved oxygen concentration of 2 mg/l (defautl value).
- ❑ Ensure a reasonable COD/N ratio.
- ❑ Ensure availability of copper ions.

Minimizing the emissions:

- ❑ Ensure a reasonable aeration time in order to minimize stripping.

2. LITERATURE REVIEW. TOOLS FOR GHG EMISSIONS EVALUATION.

➢ GHG prediction and control by means **MECHANISTIC DYNAMIC MODELLING**: the variation of wastewater characteristics, design parameters and operative parameters influences the plant performance indices.

➢ GHG emission modelling by means the **PLANT – WIDE APPROACH**: describe the behaviour of the entire WWTP including both sludge line and water line

STATE VARIABLES

- ❑ wastewater characteristics
- ❑ design parameters
- ❑ operative parameters

PERFORMANCE PARAMETERS

- ❑ effluent quality
- ❑ operative costs
- ❑ GHG emissions

Benchmark Simulation Model

- ❑ BSM1 – *Copp, 2002*
- ❑ BSM2 – *Jeppsson 2007 & Nopens, 2010*
- ❑ *BSM2G – Flores – Alsina et al. 2011, 2013*

THEY INFLUENCE THE EMISSIONS FROM BIOLOGICAL PROCESSES

PLANT - WIDE MODELLING

Corominas L. et al., 2010; Flores-Alsina X. et al., 2011, 2013; Guo L. et al., 2012; Porro J. et al., 2011; Sweetapple C. et al., 2013; Rodriguez - Garcia G. et al., 2012.

2. LITERATURE REVIEW. TOOLS FOR GHG EMISSIONS EVALUATION.

➢ GHG quantification by means site – specific or default (IPCC Guidelines) **EMISSION FACTORS** : Mass balance equations between the amount of GHG produced and wastewater treated. ***(M.B. Shahabadi et al.,2009; R. Gori et al., 2011, 2013; A. Listowski et al. ,2011; M. Préndez et al. , 2008)***

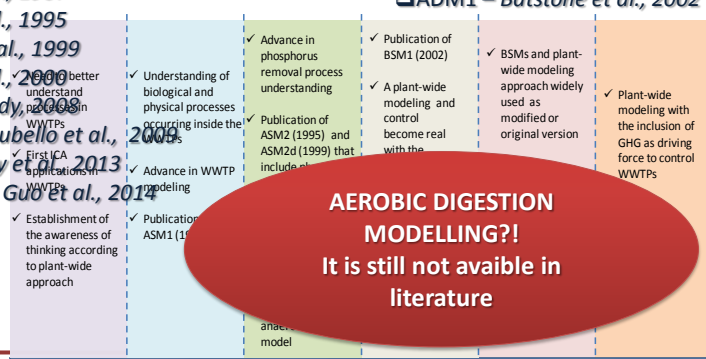
➢GHG prediction and controll by means **MATHEMATICAL MODELLING.**

Activated Sludge Model

- ❑ ASM1 – *Henze et al., 1987*
- ❑ ASM2 – *Henze et al., 1995*
- ❑ ASM2d – *Henze et al., 1999*
- ❑ ASM3 – *Henze et al., 2000*
- ❑ ASMN - *Hiatt & Grady, 2008*
- ❑ Modified ASM1 - *Lubello et al., 2009*
- ❑ ASMG1 – *Mampaey et al., 2013*
- ❑ Modified ASMG1 – *Guo et al., 2014*

Anaerobic Digestion Model

❑ADM1 – *Batstone et al., 2002*



AEROBIC DIGESTION MODELLING?!
It is still not avaible in literature

2. LITERATURE REVIEW. METHODS FOR GHG SAMPLING AND MEASUREMENT.

SAMPLING | MEASUREMENT

SAMPLING METHOD

GAS PHASE

LIQUID PHASE

Floating chamber
(Y. Law et al., 2012; E. Ugetti et al., 2012; Czepiel et al., 1995; A. Aboobakar et al., 2013; L. Ye et al., 2013; J. Desloover et al., 2011; J.H. Ahn et al., 2010).

Sampling bags
(Foley et al., 2010)

Vacuum vial
(Y. Law et al., 2012)

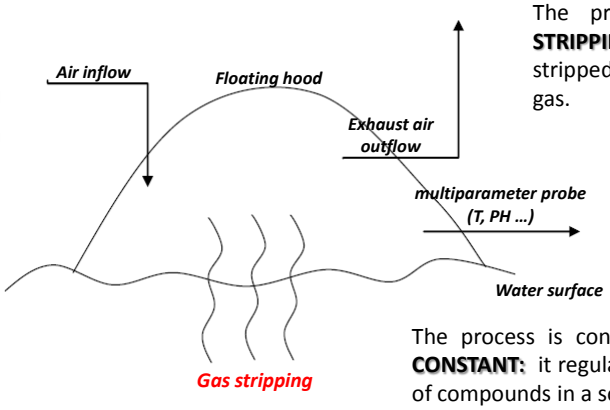
The materials are: PVC, polypropylene (PP), aluminum, Teflon (politetrafluoroetilene – PTFE), polivinilifluoride (Tedlar - PVF).

2. LITERATURE REVIEW. METHODS FOR GHG SAMPLING: The Floating Chamber

SAMPLING | MEASUREMENT

GAS PHASE SAMPLING, ***The floating chamber:***

THE MAIN METHOD FOR OFF-GAS COLLECTION FROM LIQUID SURFACE



The principle of operation is **STRIPPING**: during aeration N_2O is stripped from liquid phase into gas.

The process is controlled by **HENRY'S LAW CONSTANT:** it regulates distribution liquid/gas of compounds in a solution.

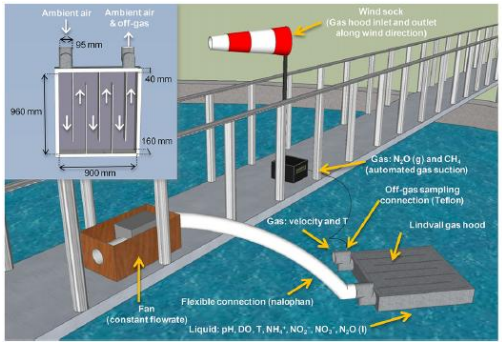
2. LITERATURE REVIEW. METHODS FOR GHG SAMPLING: The Floating Chamber

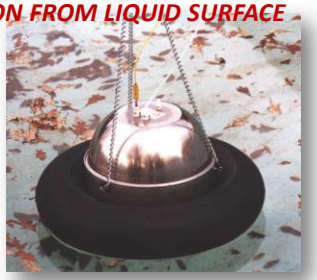
SAMPLING | MEASUREMENT

GAS PHASE SAMPLING, ***The floating chamber:***

THE MAIN METHOD FOR OFF-GAS COLLECTION FROM LIQUID SURFACE

Literature Examples.





Set-up for the on-line measurement of gaseous N_2O and CH4 emissions, with position of the liquid grab sampling and detail of the Lindvall gas hood (inset). ***(J. Desloover et al., 2011).***

2. LITERATURE REVIEW. METHODS FOR GAS SAMPLING AND MEASUREMENT.

SAMPLING | MEASUREMENT

MEASUREMENT METHOD

OFF LINE. The sample is taken on site and analyzed in lab.
(Y. Law et al., 2012; E. Ugetti et al., 2012; Foley et al., 2010; Czepiel et al., 1995)

ON LINE. Sampling and measurement are on site processes. It is possible to observe spatial and temporal variation of the observed parameter.
(A. Aboobakar et al., 2013; L. Ye et al., 2013; J. Desloover et al., 2011; J.H. Ahn et al., 2010; A. M. Lotito et al., 2012; P. Wunderlin et al., 2012; A. Joss

GAS PHASE

LIQUID PHASE

GASCHROMATOGRAPH

IR ANALYZER

MICROSENSOR

A STANDARD PROTOCOL FOR GAS SAMPLING and MEASUREMENT from WWTPs is still not avaible in literature

2. LITERATURE REVIEW. METHODS FOR GAS SAMPLING AND MEASUREMENT.

SAMPLING | MEASUREMENT

OFF LINE MEASUREMENT FOR BOTH LIQUID AND GAS PHASES.

The samples are taken from the floating chamber or sampling bag through nylon syringes (20 or 30 ml). They are analyzed by a **GASCHROMATOGRAPH.**

Agilent 6890N Network Gas

Varian 450-GC

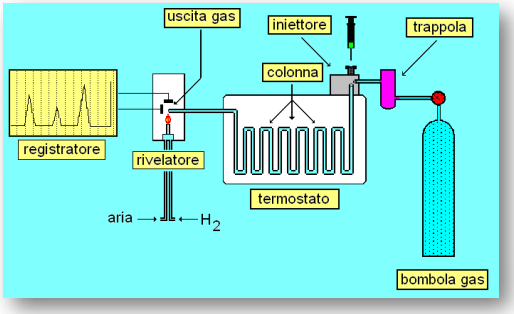
(E. Ugetti et al., 2012; M.J. Kampschreur et al., 2009) .

2. LITERATURE REVIEW. METHODS FOR GAS SAMPLING AND MEASUREMENT.

SAMPLING | MEASUREMENT

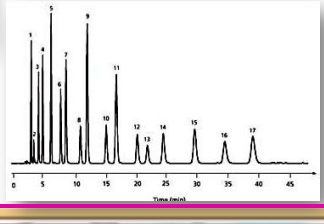
OFF LINE MEASUREMENT FOR BOTH LIQUID AND GAS PHASES.

Principle of operation of the gaschromatograph



PRINCIPLE OF OPERATION:
It consists in separating the different components of a mixture

Output
CHROMATOGRAM



2. LITERATURE REVIEW. METHODS FOR GAS SAMPLING AND MEASUREMENT.

SAMPLING | MEASUREMENT

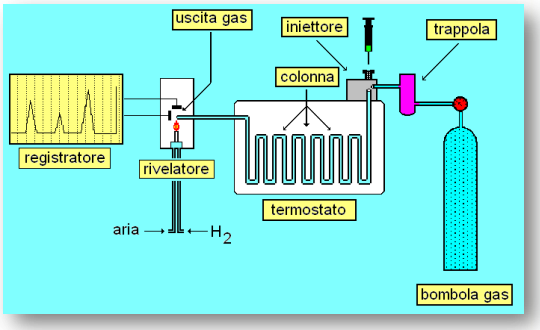
OFF LINE MEASUREMENT FOR BOTH LIQUID AND GAS PHASES.

Principle of operation of the gaschromatograph

INJCTOR . The gas or liquid mixture is introduced in the column.

CYLINDER. It contains the carrier gas (mobile phase), nitrogen or argon.

COLUMN. It contains the stationary phase.



DETECTOR. The electric signal is proportional to compounds concentration.

RECORDER. It provides the chromatogram.

2. LITERATURE REVIEW. METHODS FOR GAS SAMPLING AND MEASUREMENT.

SAMPLING | MEASUREMENT

OFF LINE MEASUREMENT FOR BOTH LIQUID AND GAS PHASES.

Principle of operation of the gaschromatograph

Electron Capture detector

INSTRUMENT SETTING
Background signal

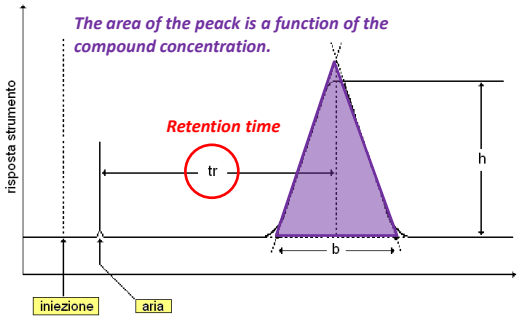
$$N_2 \longrightarrow N_2^+ + e^-$$

ELECTRIC SIGNAL PRODUCTION

When an external compound crosses the column the following reactions are provided:

$$A + e^- \longrightarrow A^-$$

$$A^- + N_2^+ \longrightarrow AN_2^+$$



2. LITERATURE REVIEW. METHODS FOR GAS SAMPLING AND MEASUREMENT.

SAMPLING | MEASUREMENT

ON LINE SAMPLING FOR GAS PHASE.

An **INFRARED ANALYZER** is used during on line sampling: ***Multi-gas Analyzer FT.IR(Fourier Transform Infrared Spectroscopy) .***

FT.IR Gas Analyzer GASMET CX – 4000 (***P. Wunderlin et al., 2012; A. Joss et al., 2009).***

Infrared Gas Analyzer. Teledyne API Model 320E. ***(J.H.Ahn et al., 2010).***

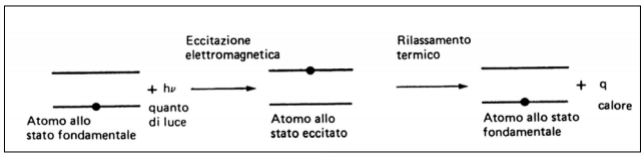
The Furier Transform is a function that transforms signals in frequencies.

2. LITERATURE REVIEW. METHODS FOR GAS SAMPLING AND MEASUREMENT.

SAMPLING | MEASUREMENT

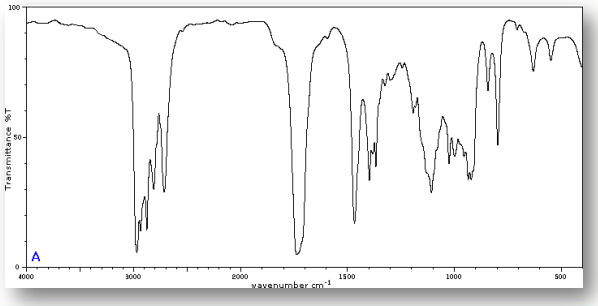
ON LINE SAMPLING FOR GAS PHASE

Principle of operation of the Multi-gas Analyzer FT.IR



PRICIPLE OF OPERATION:
e.m. radiation – matter interaction

Output:
INFRARED SPECTRUM

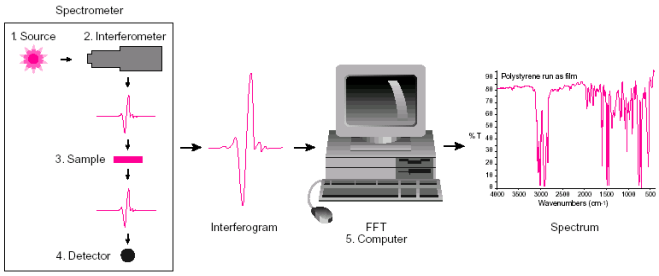


2. LITERATURE REVIEW. METHODS FOR GAS SAMPLING AND MEASUREMENT.

SAMPLING | MEASUREMENT

ON LINE SAMPLING FOR GAS PHASE

Principle of operation of the Multi-gas Analyzer FT.IR



SOURCE. Infrared radiation source (Incandescent lamp).

INTERFEROMETER. Michelson Interferometer

SAMPLE.

DETECTOR. It transforms energy into electric signal

COMPUTER. It provides the Furier Transform .

2. LITERATURE REVIEW. METHODS FOR GAS SAMPLING AND MEASUREMENT.

SAMPLING | MEASUREMENT

ON LINE SAMPLING FOR LIQUID PHASE

Clark –type microsensor

Microsensor - UNISENSE ***(Y. Law et al., 2012)*** . http://www.unisense.com/N2O)

Principle of operation

Driven by the external partial pressure, nitrous oxide from the environment will penetrate through the sensor tip membrane and be reduced at the metal cathode surface . The picoammeter converts the resulting reduction current to a signal .

3. LITERATURE ANALYSIS. STRENGTHS.

1. The knowledge on CO_2 and CH_4 formation during biological processes is very rich.
2. The knowledge N_2O formation during nitrification, denitrification and nitrifier denitrification processes is increased.
3. The infleunce of design variables on amount of emissions is clear.
4. The knowledge on modelling about activated sludge processes (ASM) with nitrous oxide emissions is increased.

3. LITERATURE ANALYSIS. WEAKNESSES.

1. Lacking of a comprehensive standard protocol for gas sampling and measurement in liquid and gas phase
2. Lacking of a model for sludge aerobic digestion
3. Lacking of experimental measurement at pilot scale and full scale of thickening and aerobic digestion

Università degli Studi della Basilicata
Greenhousegases production in wastewater treatment plants
Activated sludge: 100 *plus* 1 years – Palermo, 11 Maggio 2015

Thank you very much for your attention

Donatella CANIANI, donatella.caniani@unibas.it

Marianna CAIVANO, marianna.caivano@unibas.it

5. PRELIMINARY RESULTS. Develop a protocol for gas sampling and measurement.

Technical and economic evaluations

1. The **Gas Analyzer IR is inadeguate for gas measuring**: it is sensitive to humidity and temperature variations, so the data could be inaccurate. Furthermore, it is more expensive **(60 000 – 80 000 euros).**
2. The gas sampling directly from the **hood using syringes is not adequate** because of they are expensive (**180 euros/cad**). So the use of sampling bags with a pump from hood to portable gascromatogrph (miniGC) is better.
3. **ALUMINUM BAG IS BETTER THAN TEDLAR ONE** BECAUSE IT AVOIDS THE FORMATION OF MOISTURE . Furthermore, it is cheap (**4 euros/0.5 L**), reusable and more resistent.
4. **A passive sampler** (**10 euros/cad**) with a minimum sampling time of 8 hours **is useful** to provide the magnitude of gas concentrations.
5. **Syringes (25 ml) with silice gel can be use** in place of aluminum bags. They can be link to the GC using a drip tube with closed infusion set.

7. FUTURE DEVELOPMENTS.

- Build the aerobic digestion tank
- Develop a modified Activated Sludge Model for aerobic digestion
- Start – up of the hood for the off-gas collection and preliminary results about gas sampling and measurement from full-scal aerobic digestion tank.