Corso di formazione - La depurazione degli scarichi industriali

19-21 novembre 2019

# La rimozione di azoto da reflui della stampa digitale tessile - studi in corso nel progetto LIFE DeNTreat

**Roberto Canziani -** Politecnico di Milano Dipartimento di Ingegneria Civile e Ambientale (DICA) Sezione Ambientale

**Giovanni Bergna –** Lariana Depur S.p.A.

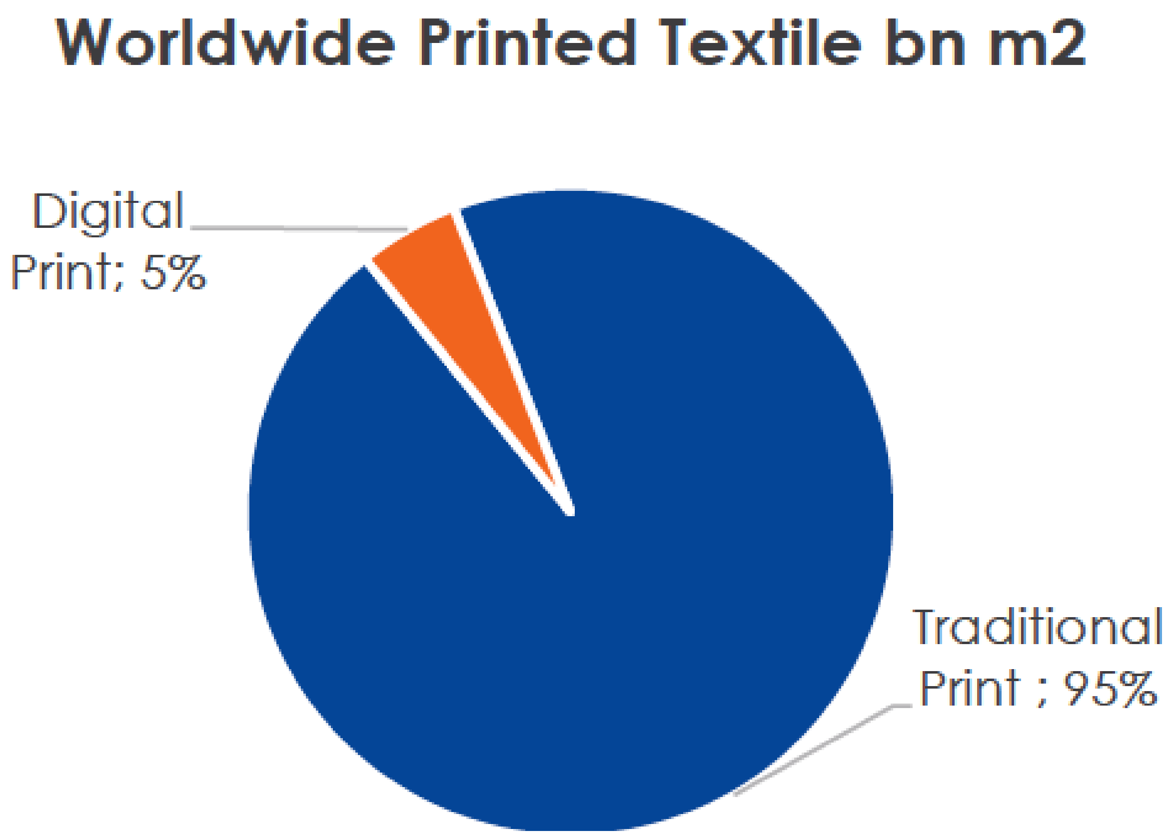
This work has received funding from the Project LIFE ENV/IT/000345 “LifeDeNTreat”, with the contribution of the LIFE Programme of the European Union

# BACKGROUND
# Global growth of Digital Textile Printing (DTP)

DTP has spread globally due to its versatility with respect to conventional printing techniques.

**The EU-LIFE DeNTreat project focuses on PN/anammox process as a decentralized treatment for ink-jet textile printing wastewater**

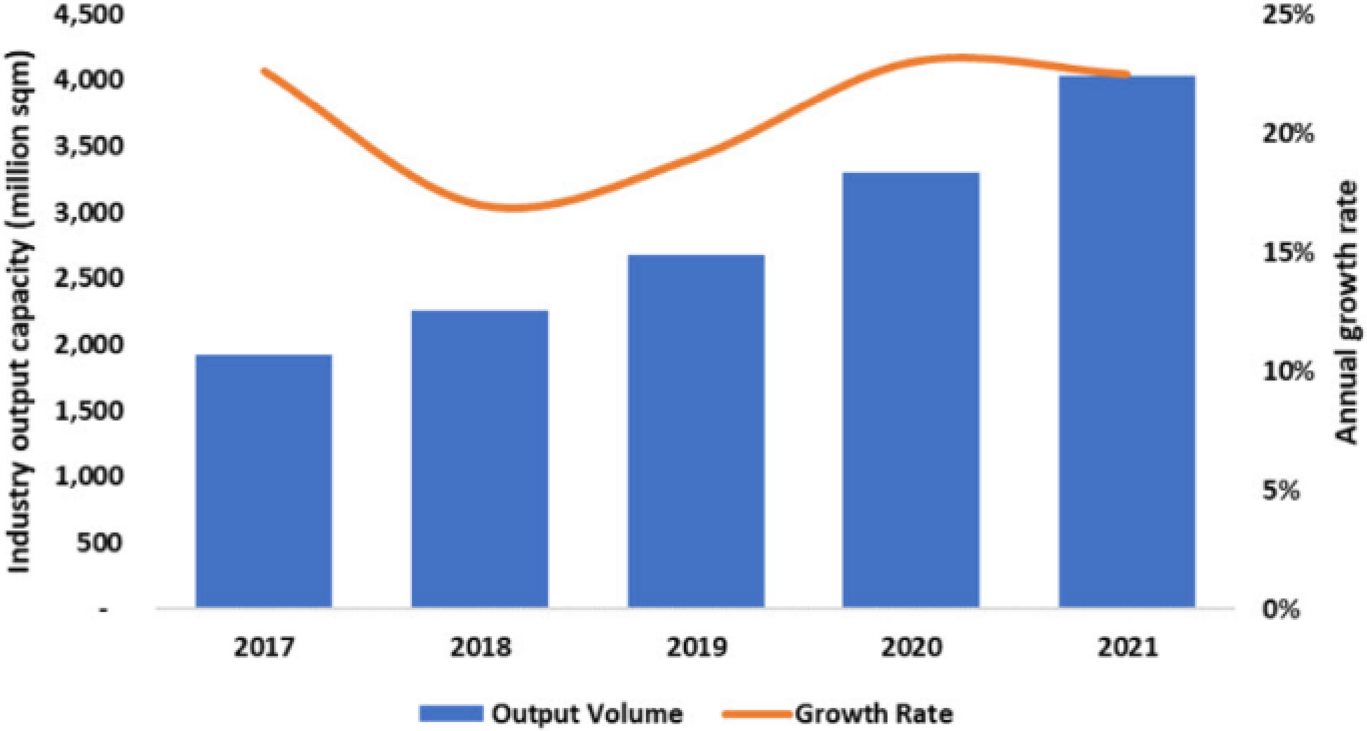
# BACKGROUND
## Global growth of Digital Textile Printing (DTP)




Source: Menderes 2017

- In **2017**, digital textile printing has a worldwide market share of about **5%.**

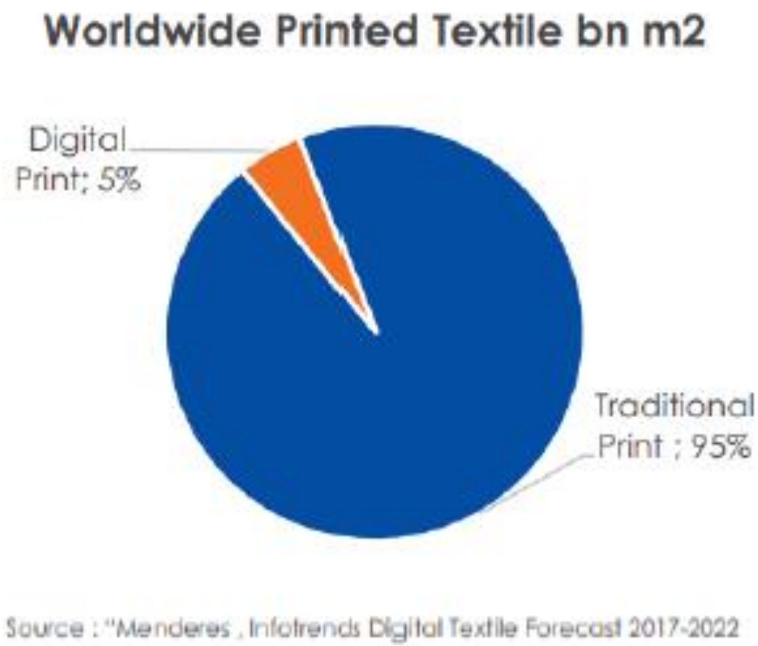
# BACKGROUND
## Global growth of Digital Textile Printing (DTP)

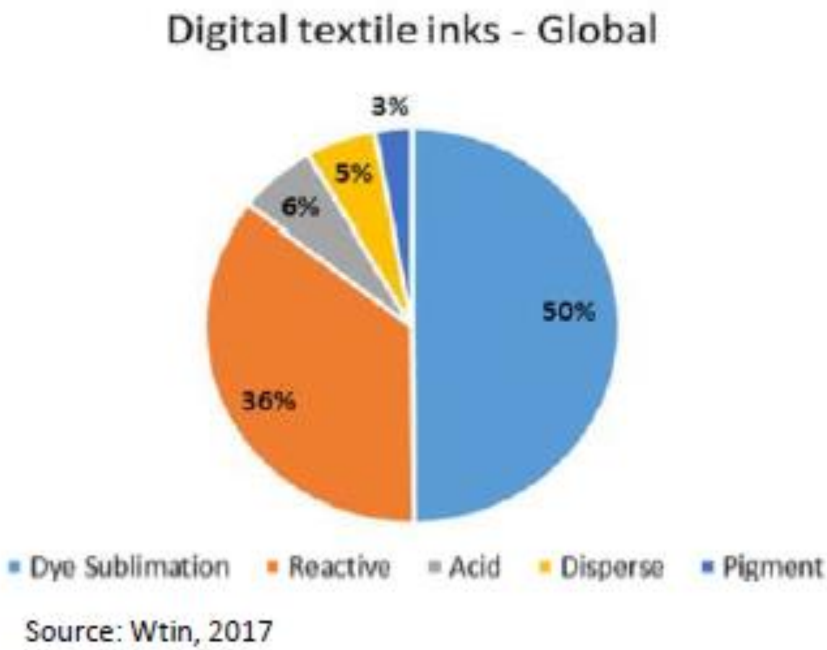



Source: Wtin, 2017

- In **2017** ,over **1.9 billion sqm** of fabric were digitally printed .
- The **annual growth rate** of digital textile textile printing is projected to **20 %** by volume through the period 2017 -2021.

# BACKGROUND
# Global growth of Digital Textile Printing (DTP)



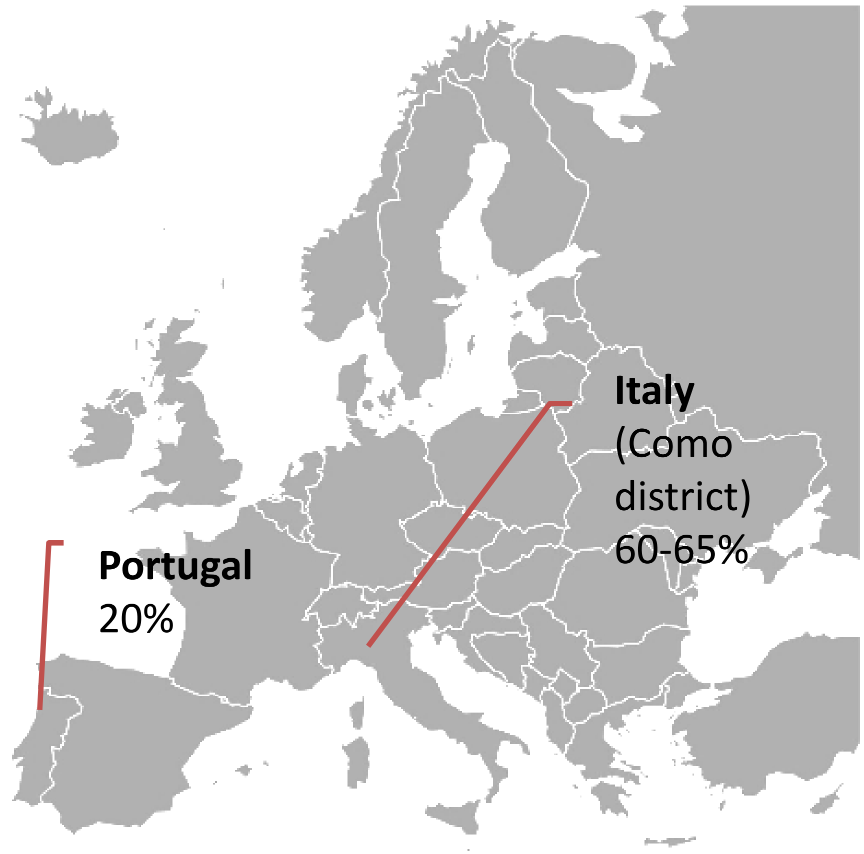




- Worldwide, digital textile printing has a **market share** of about **4-5%.**
- **Dye-sublimation ink** is the most consumed ink type, with a **50 % share** .
- **Reactive ink** follows with a **36 % share**.

# BACKGROUND
# Global growth of Digital Textile Printing (DTP)

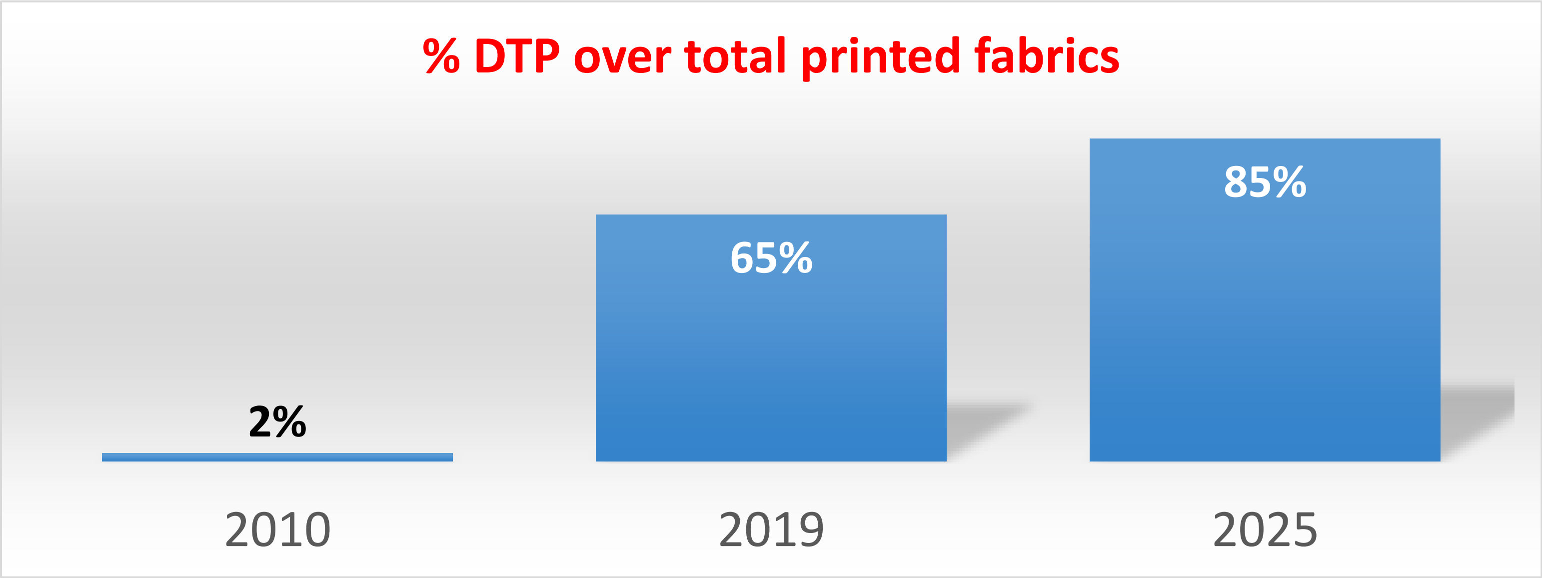
Digital textile printing growth in the last 15 years:

Average in Europe:
**25%**



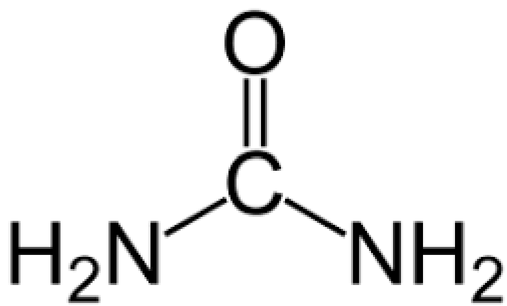
# BACKGROUND
# Global growth of Digital Textile Printing (DTP)

## Como textile industrial district:




In the Como district, adoption of digital printing is one response to the difficulties in the textile sector linked to the global crisis.

# BACKGROUND
# Global growth of Digital Textile Printing (DTP)



Urea

Urea
- Increases water solubility of dyes
- Enhances brightness and intensity of dyes

<u>Limited water consumption</u>

BUT

**N-rich discharges i.e. <u>150 to 600 mg N/L</u>**

# BACKGROUND
## Nitrogen: a new problem

DTP: new problems from pollution related to the printing process.

DTP produces (compared with traditional printing techniques)

- **lower volumes of wastewater**
- **lower COD and colour load**
- **higher N concentration** (urea and ammonium from acid and reactive dyes (150 to 600 mgN/L)
- **lower COD/N ratio** (about 2 gCOD/gN).

DTP makes printing more flexible, but is responsible of an increase of **more than 200% of Nitrogen content in wastewater**.

# BACKGROUND
## Nitrogen: a new problem

- DTP needs pre-treatments of the fabric: different characteristics of the dyes used compared to traditional printing pastes.
- Some ingredients of the traditional printing pastes have to be put over the fabric before printing.
- In particular: urea, the dye fixer compound, is applied in a pre-treatment process and needs impregnation of 100% of the to-be-printed fabric
- in traditional printing technologies, just the areas to be printed are actually treated with urea. This drastically increases the amount of urea used (kg urea per $m^2$ of fabric).
- Urea is then (almost completely) washed out after printing and goes into the wastewater.

# WASHING BLOCK DIAGRAM (an example)

**L6 – Lavaggio stampa digitale emulsione Tipo 3**

| | |
|---|---|
| Reparto | Lavaggio stampati |
| Tessuto | Seta |
| **Processo** | **Lavaggio stampa Ink-Jet emulsione Tipo3** |
| Macchina | Lavaggio in corda |
| Item | LC |
| Durata del ciclo (min.) | 50 |
| Numero di cicli/anno | 13,51 |
| Tessuto lavorato (mt./anno) | 10136 |
| Tessuto lavorato per ciclo (mt.) | 750 |

| | | |
|---|---|---|
| **Acqua greggia** | 1° Lavaggio<br>T=20°C<br>t=10 min | **Scarico:**3300 litri<br>*COD [mg/l]= 5.804*<br>*Norg [mg/l]= 8.668,8*<br>*NH4-N [mg/l]= 36* |
| **Acqua addolcita** | 2° Lavaggio<br>T=60°C<br>t=10 min | **Scarico:** 3300 litri<br>*COD [mg/l]= 1.508*<br>*Norg [mg/l]= 2.133*<br>*NH4-N [mg/l]= 9* |
| **Acqua addolcita** | 3° Lavaggio<br>T=90°C<br>t=10 min | **Scarico:**3300 litri<br>*COD [mg/l]= 1.015*<br>*Norg [mg/l]= 239,4*<br>*NH4-N [mg/l]= 1,8* |
| **Acqua greggia** | 1° Risciacquo<br>T=20°C<br>t=5 min | **Scarico:** 3300 litri<br>*COD [mg/l]= 653*<br>*Norg [mg/l]= 117*<br>*NH4-N [mg/l]= 0* |
| **Acqua addolcita** | 4° Lavaggio<br>T=90°C<br>t= 10 min | **Scarico:** 3300 litri<br>*COD [mg/l]= 462*<br>*Norg [mg/l]= 63*<br>*NH4-N [mg/l]= 0* |
| **Acqua greggia** | 2° Risciacquo<br>T=20°C<br>t=5 min | **Scarico:** .3300 litri<br>*COD [mg/l]= 111*<br>*Norg [mg/l]= 14,4*<br>*NH4-N [mg/l]= 0* |

Wastewater
8000-9000 mgN/l

0 mgN/l

# THE PREVIOUS TARIFF

$$T_2 = F_2 + \{f_2 + dv + K_2 \left[ \frac{O_i}{O_f} (db + Mdb + df + 1/3\ df + Mdf) \right] + da + daN \}\ V$$

daN = cost coefficient of charges for the nitrogen treatment (0,03369 €/m$^3$)

+

Fee for limit derogation (over 100 mgN/l) = 0,75 €/kgN

Wastewater with 200 mgN/l, 1.000 mg COD/l, BOD 350 mg/l, 100 mgSST/l

Total tariff for ww treatment = 1,5809 + 0,075 = 1,6559 €/m$^3$

Fee for N = 0,03369 + 0,075 = 0,10869 €/m$^3$

Fee for N = 0,5435 €/kgN

# THE NEW TARIFF

ARERA - DELIBERAZIONE 28 SETTEMBRE 2017 665/2017/R/IDR APPROVAZIONE DEL TESTO INTEGRATO CORRISPETTIVI SERVIZI IDRICI (TICSI), RECANTE I CRITERI DI ARTICOLAZIONE TARIFFARIA APPLICATA AGLI UTENTI

$$T_p^{ATO} = QF_p^{ATO} + QC_p^{ATO} + QV_p^{ATO} \cdot V_p$$

$$QV_p^{ATO} = Tf_{ind}^{ATO} + \max\left\{1; \left[\begin{array}{l} \%_{COD} \cdot \frac{COD_p}{COD_{rif}} + \%_{SST} \cdot \frac{SST_p}{SST_{rif}} + \%_N \cdot \frac{N_p}{N_{rif}} + \\ + \%_P \cdot \frac{P_p}{P_{rif}} + \sum_j \%_{X,j} \cdot \frac{X_{j,p}}{X_{j,rif}} \end{array}\right]\right\} \cdot Td_{ind}^{ATO}$$

Nrif = 10 mg/l

%N = 15

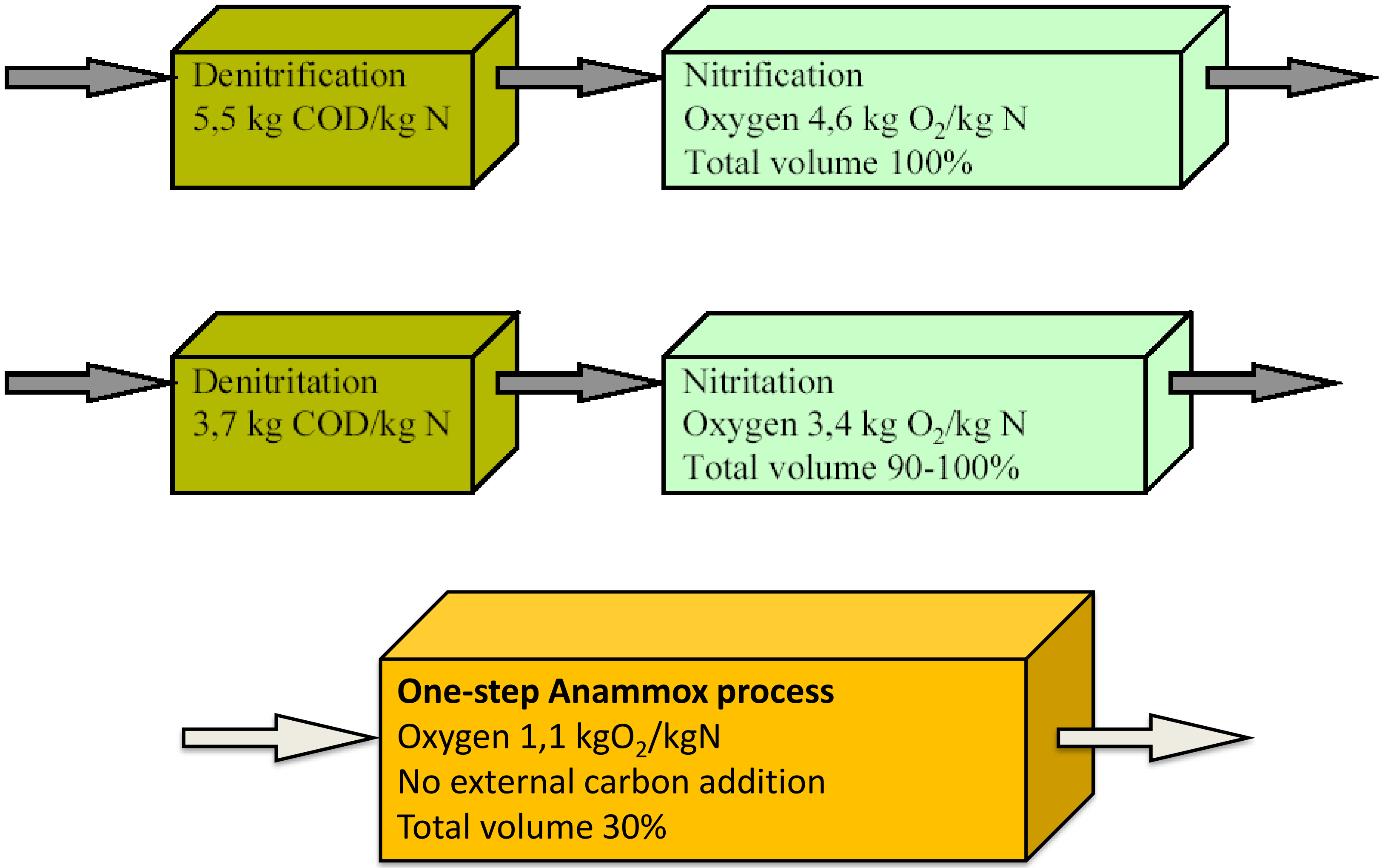
Wastewater with 200 mgN/l, 1.000 mg COD/l, BOD 350 mg/l, 100 mgSST/l

Total tariff for ww treatment = 2,1166 €/m$^3$ (+28%)

**Fee for N = 0,9270 €/m$^3$ (8,5 times the previous tariff)**

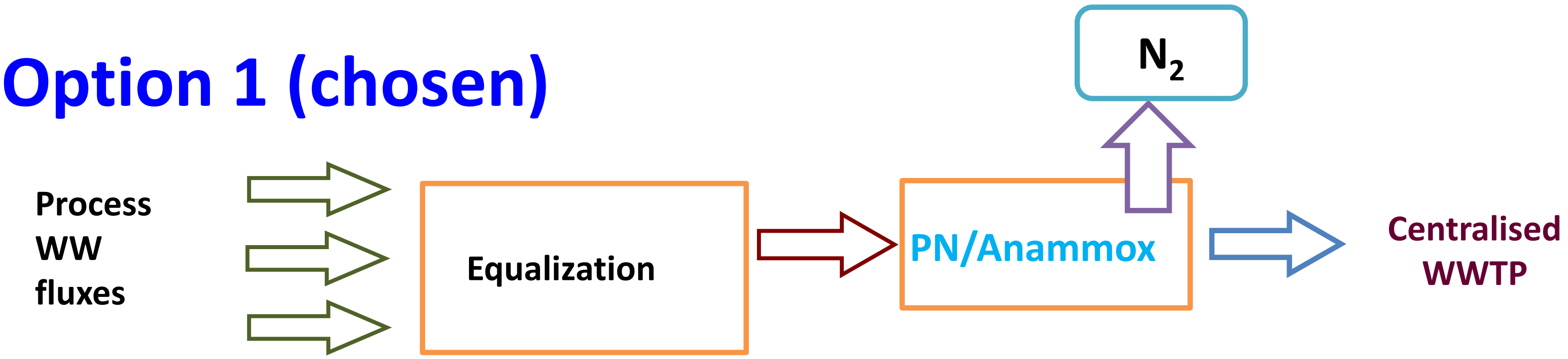
**Fee for N = 4.635 €/kgN (8,5 times the previous tariff)**

# The concept

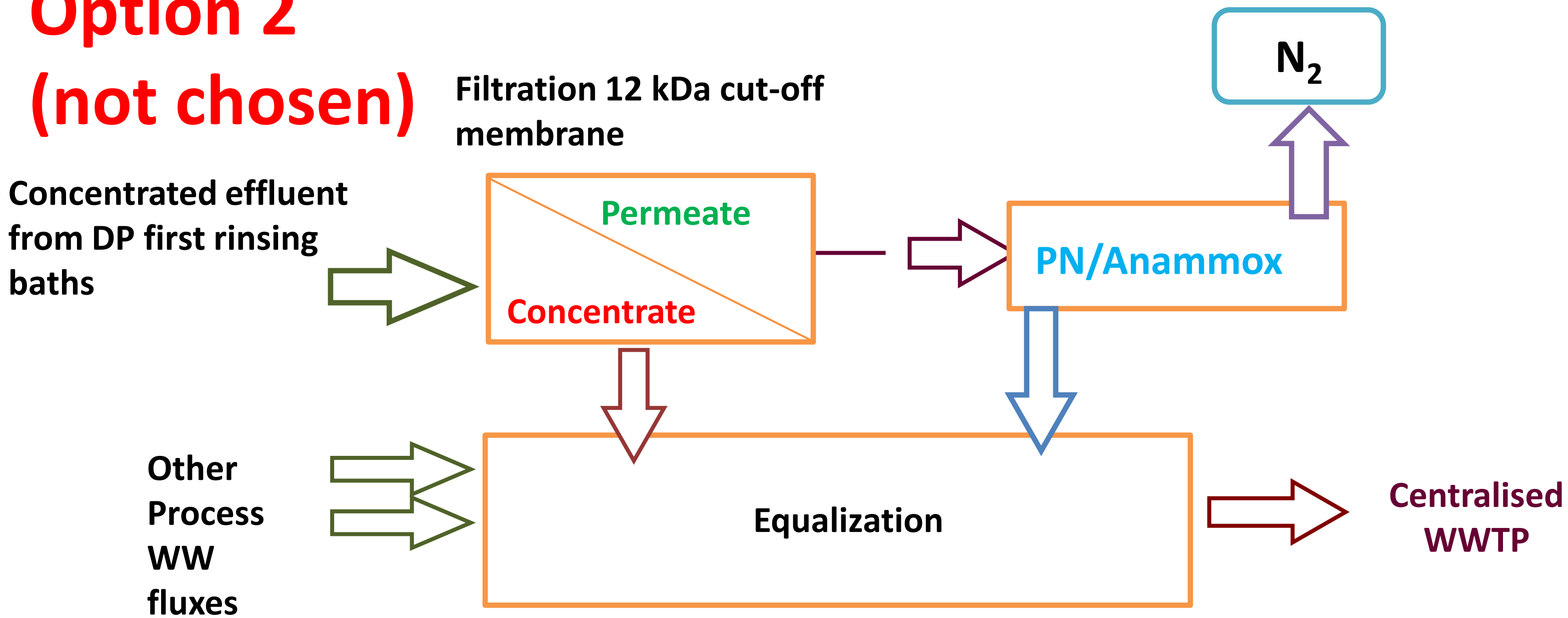

Denitrification
5,5 kg COD/kg N
Nitrification
Oxygen 4,6 kg $O_2$/kg N
Total volume 100%
Denitritation
3,7 kg COD/kg N
Nitritation
Oxygen 3,4 kg $O_2$/kg N
Total volume 90-100%
**One-step Anammox process**
Oxygen 1,1 kg$O_2$/kgN
No external carbon addition
Total volume 30%

# The concept

## Option 1 (chosen)




## Option 2 (not chosen)



Life DeNTreat

# LIFE16 ENV/IT/000345

Develop sustainable solutions to deal increasing nitrogen concentrations in industrial discharges of digital textile printing (DTP).

- ❑Phase 1 preliminary study (October 2014 – June 2015)
- ❑Phase 2 continuous laboratory pilot plant (July 2015 – April 2016)
- ❑Phase 3 Life project - demonstration plant (July 2017 – in progress)

**Phase 1 and Phase 2**

supported by Unindustria Como, Confindustria Lombardia, Sistema Moda Italia, Comodepur, Consorzio Alto Seveso and Livescia

UNINDUSTRIA COMO

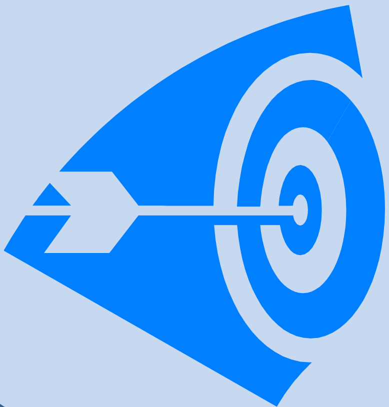
Phase 3 – LIFE project (5 members of the Consortium)

EURATEX THE EUROPEAN APPAREL AND TEXTILE CONFEDERATION

STAMPERIA DI CASSINA RIZZARDI

citeve TEXTILE TECHNOLOGY

# PROJECT AIM



**An on site wastewater treatment module using PN/Anammox** (Partial Nitritation + Anaerobic AMMonium OXidation) technology will reduce nitrogen contents of wastewaters resulting from the **DTP process by 50% to 75% ($N_{out}$ < 100 mg/l)**

More:

- to accomplish Directive 91/271/EEC art.5 requirements (> 75% removal of the overall N load of an urban catchment)
- to ensure residual nitrogen concentration in WWTP discharges (< 10 mg/l) and
  - ✓ save up to 40% in investment and operational costs (aeration)
  - ✓ reduce $N_2O$ emissions of the biological treatment to less than 20% of the currently adopted technologies
  - ✓ reduce sludge production to less than 25% of the currently adopted technologies.

# Consequences of the Life DeNTreat on the tariff: an example

DTP Wastewater:
200 mgN/l, 1.000 mg COD/l, BOD 350 mg/l, 100 mgSST/l

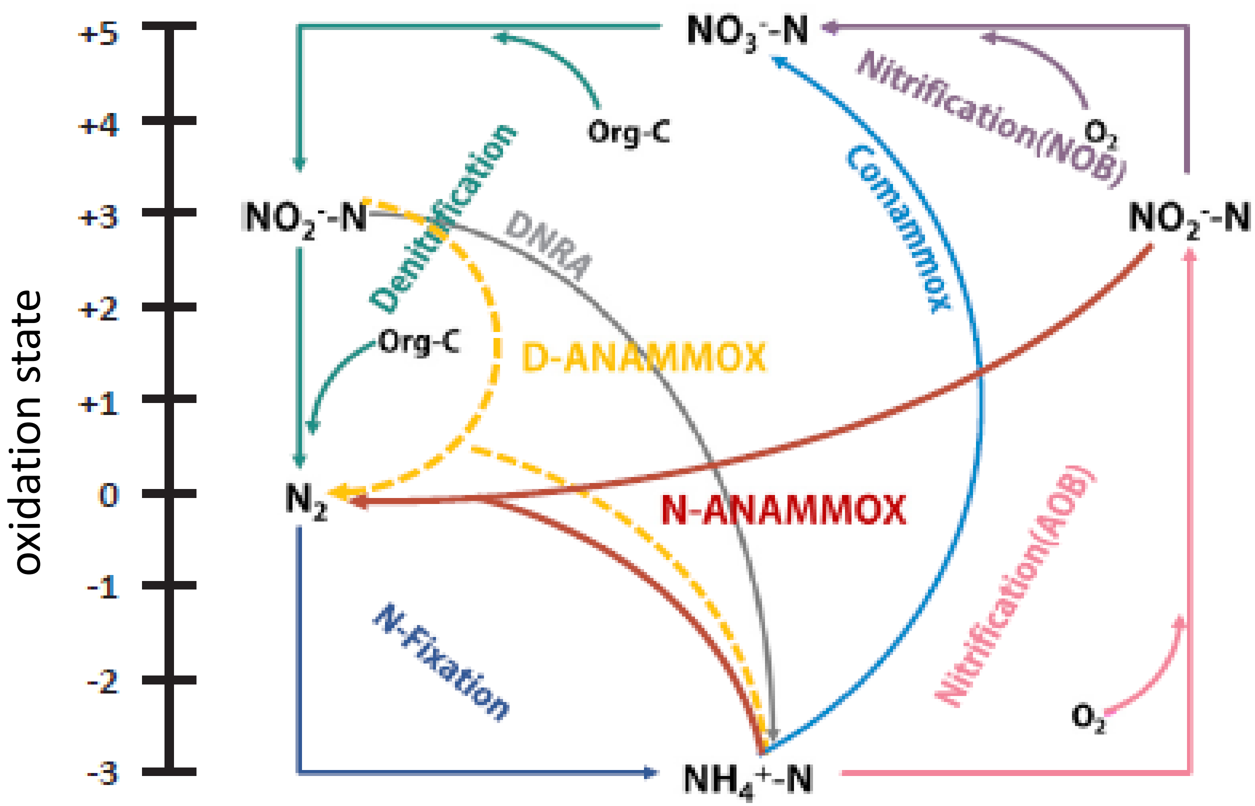
Total tariff for ww treatment = 2,1166 €/m$^3$

DTP Wastewater after treatment by Life DeNTreat technology:
50 mgN/l, 700 mg COD/l, BOD 50 mg/l, 100 mgSST/l

Total tariff for ww treatment = 1,2731 €/m$^3$

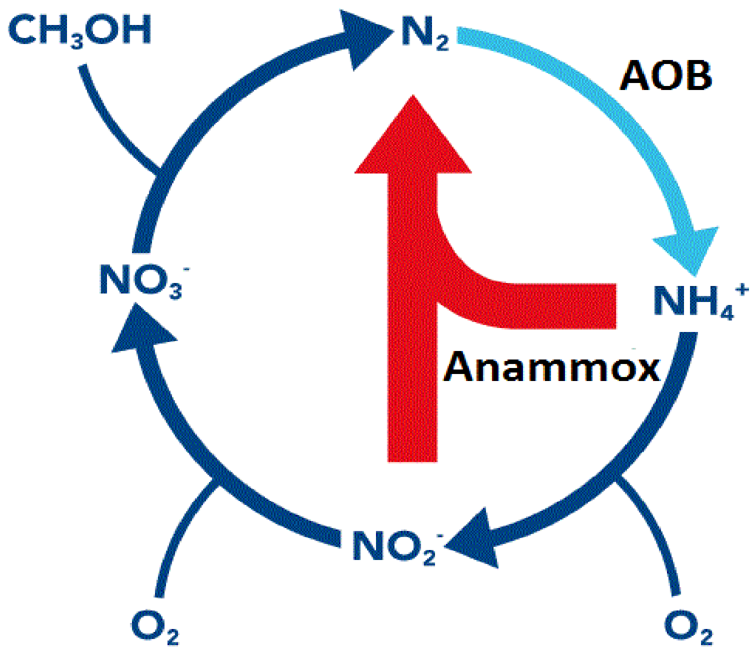
**tariff difference for ww treatment = 0,8435 €/m$^3$**

# The PN/A process – biological background




**Many bacterial populations are involved:** **anaerobic ammonia oxidation bacteria** (AnAOB), **ammonia-oxidizing bacteria** (AOB), **nitrite oxidizing bacteria** (NOB), and **heterotrophic bacteria** (HB). Cooperation and competition among the key functional microbes are critical to the stability and performance of anammox process.

# The PN/A process – biological background




AOB

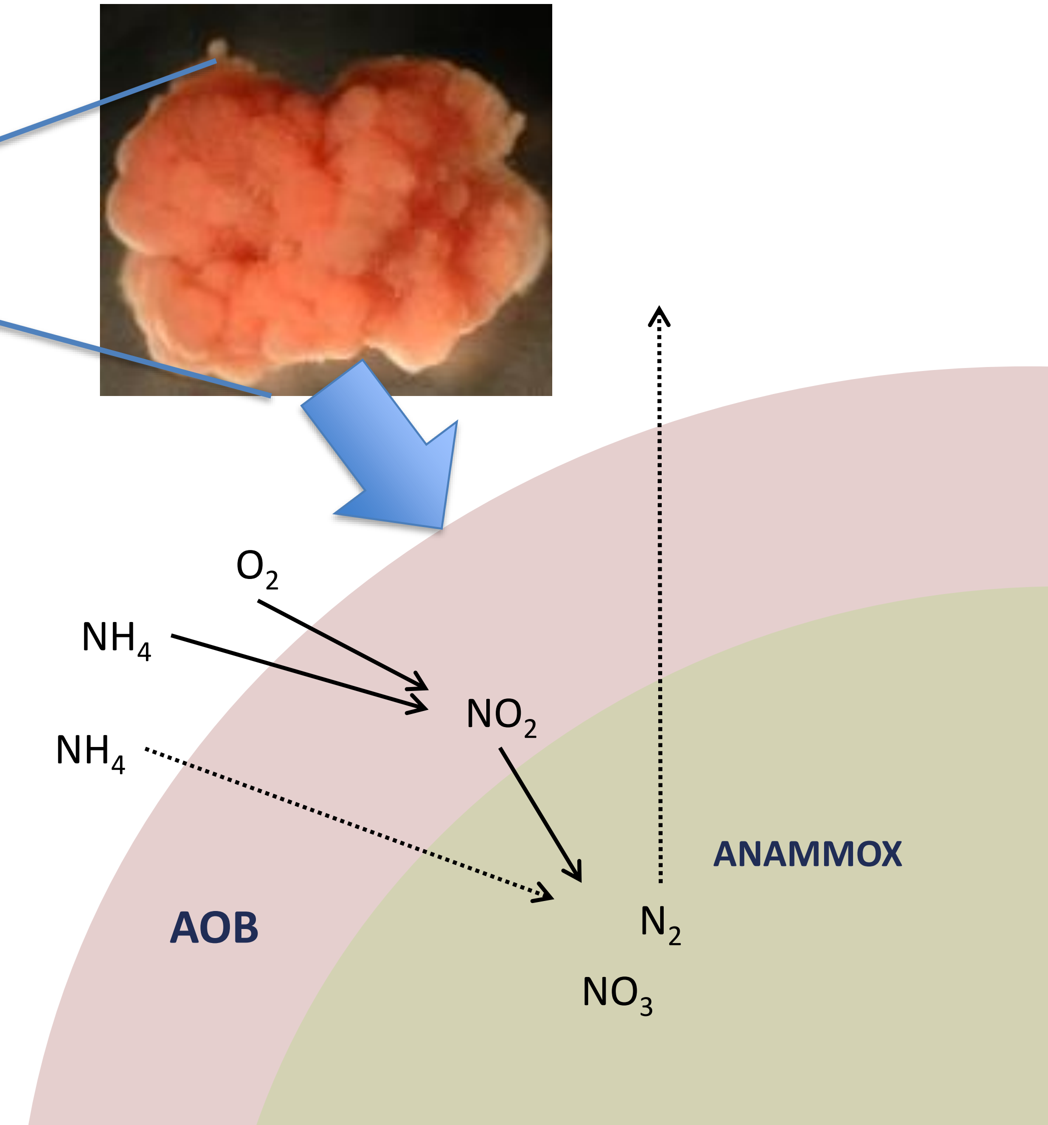
$$2NH_4^+ + 3O_2 \rightarrow 2NO_2^- + 4H^+ + 2H_2O$$

Anammox

$$NH_4^+ + 1.32NO_2^- + 0.066HCO_3^- + 0.13H^+ \rightarrow 1.02N_2 + 0.26NO_3^- + 0.066CH_2O_{0.5}N_{0.15} + 2.03H_2O$$

# The PN/A process – biological background

≈ 1 – 2 mm




Crucial process variables:
Temperature
DO
pH
$NH_4^+$ and $NO_2^-$

# DeNTreat solution: background

## Batch test for Anammox activity

(Scaglione et al., 2009; Lotti et al., 2012; Bellandi et al., in preparation)

*AOB activity testing by a pH/DO-stat titrator (left).*
*Manometric AAO activity testing (centre and right)*

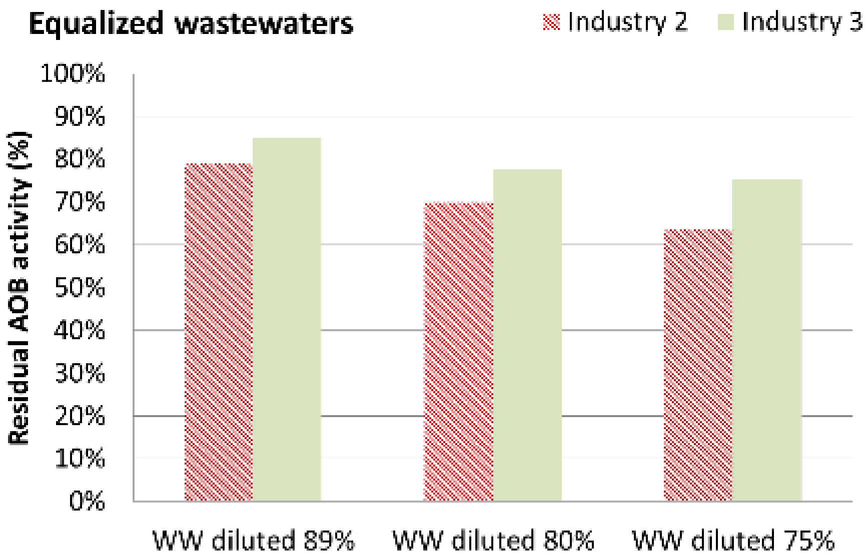
# Lab test results

Application of “PN – Anammox” on filtered concentrated streams

| | Industry 1 | | Industry 2 | | Industry 3 | |
|---|---|---|---|---|---|---|
| | Waste water | permeate | Waste water | permeate | Waste water | permeate |
| **pH** | 9.8 | | 8.9 | | 9.3 | |
| **COD** | 4 580 | 2 500 | 720 | 168 | 4 200 | 1 450 |
| **TKN** | **5 650** | **5 300** | **786** | **437** | **2 550** | **2 380** |
| **$NH_4$-N** | **38.0** | **39.6** | **8.0** | **6.5** | **22.9** | **23.3** |

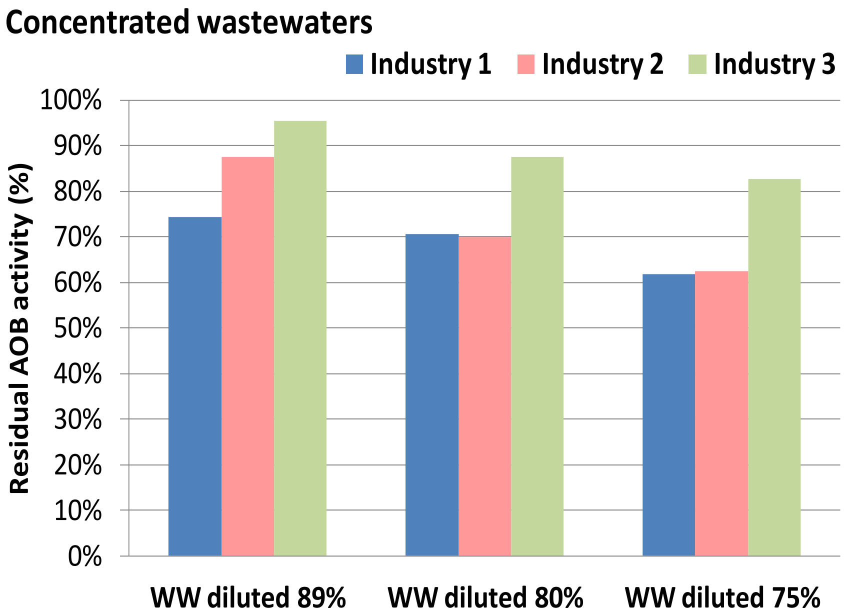
# Lab test results

Application of "PN – Anammox" on both concentrate and equalized stream



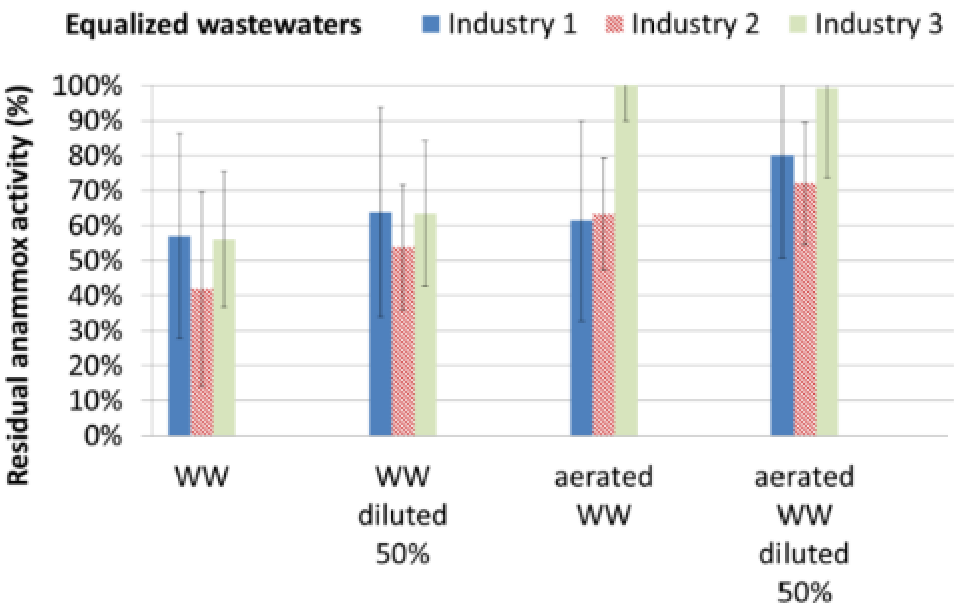

AOB do not show significant inhibition

Dilution simulates real concentrations in the completely mixed reactor, with effluent concentration less than 25% of influent concentration

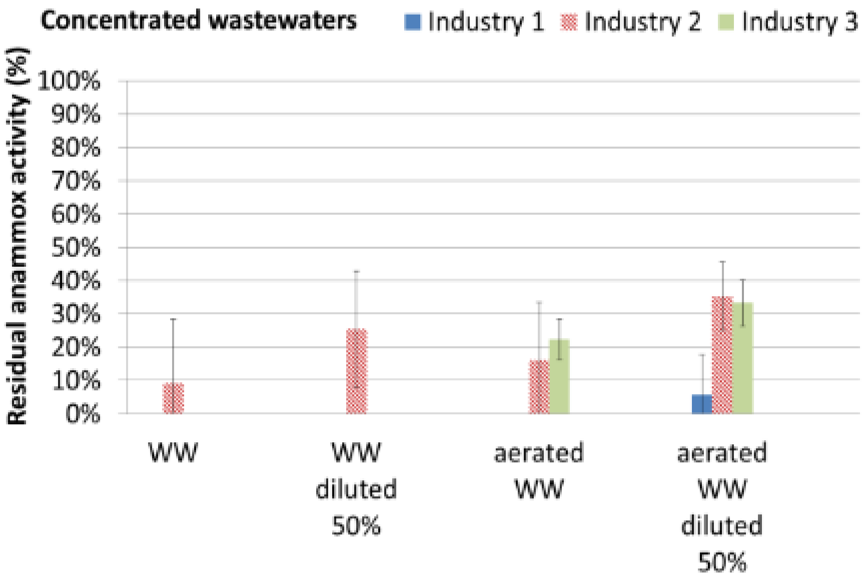


# Lab test results

Application of "PN – Anammox" on both concentrate and equalized stream

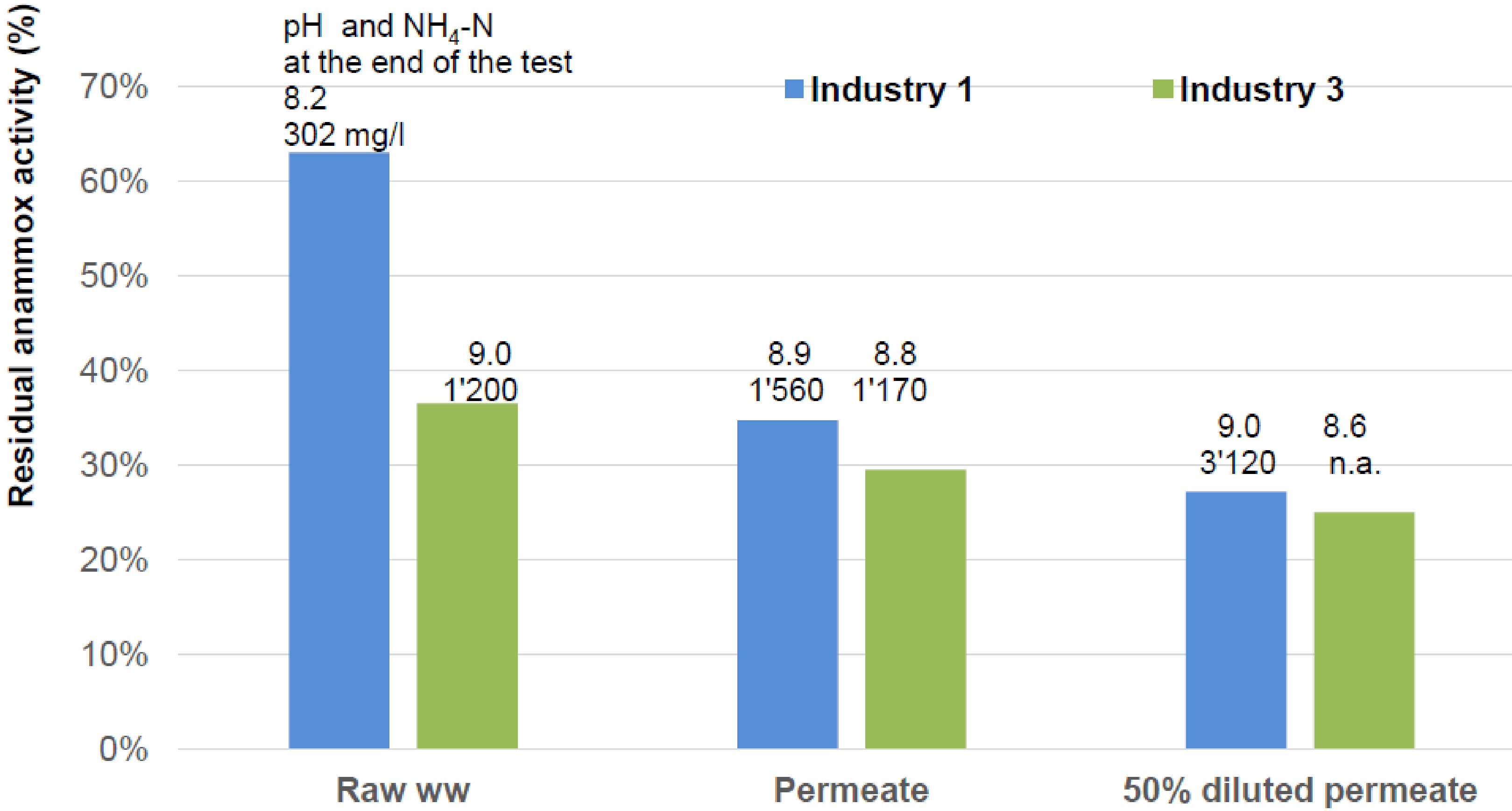



Anammox are OK in equalized WW, but reduce their activity when severely if exposed to concentrated WW, that develop high pH



# Lab test results

Application of “PN – Anammox” on concentrated streams




- Urea is hydrolysed to $NH_3$ in the batch tests.
- Accumulation of free ammonia is toxic

# Lab test results

## Ureolysis

- much of the nitrogen is under the form of UREA: $CO(NH_2)_2$
- some AOB under microaerobic conditions can develop ureolytic enzymes (urease) that quickly decompose urea into ammonia:

$$CO(NH_2)_2 + 3\,H_2O \xrightarrow{\text{urease enzyme}} 2\,NH_3 + H_2O + CO_2 \longrightarrow 2NH_4^+ + CO_3^{--}$$

- this reaction causes a pH increase

- For highly concentrated effluents with low $N\text{-}NH_4^+$ /TKN ratios, acidification due to nitritation will balance the pH rise due to urea conversion to $NH_4^+$

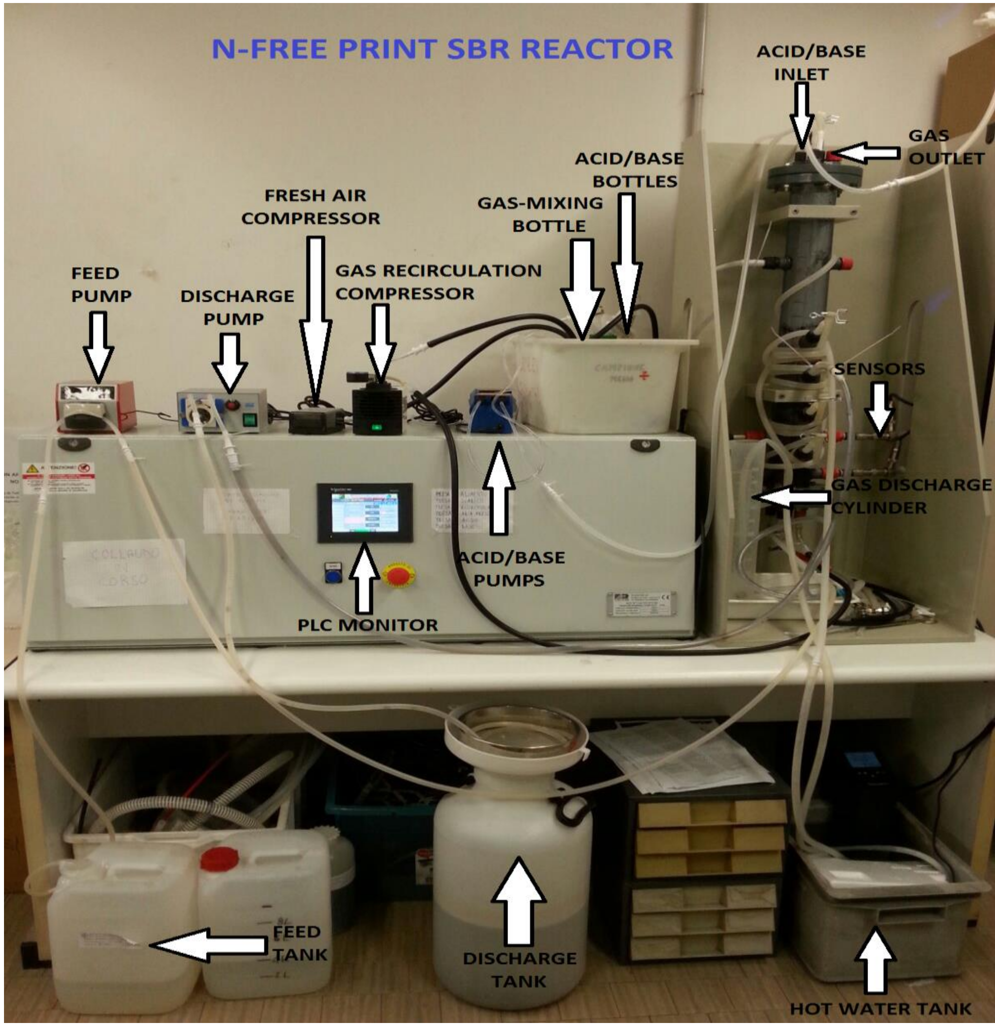
- If the raw effluent has inhibiting compounds, removal rates will be low; acclimation means bacteria become able to deompose the inhibiting compounds

- Also, free ammonia may accumulate at high pH values and inhibit the process

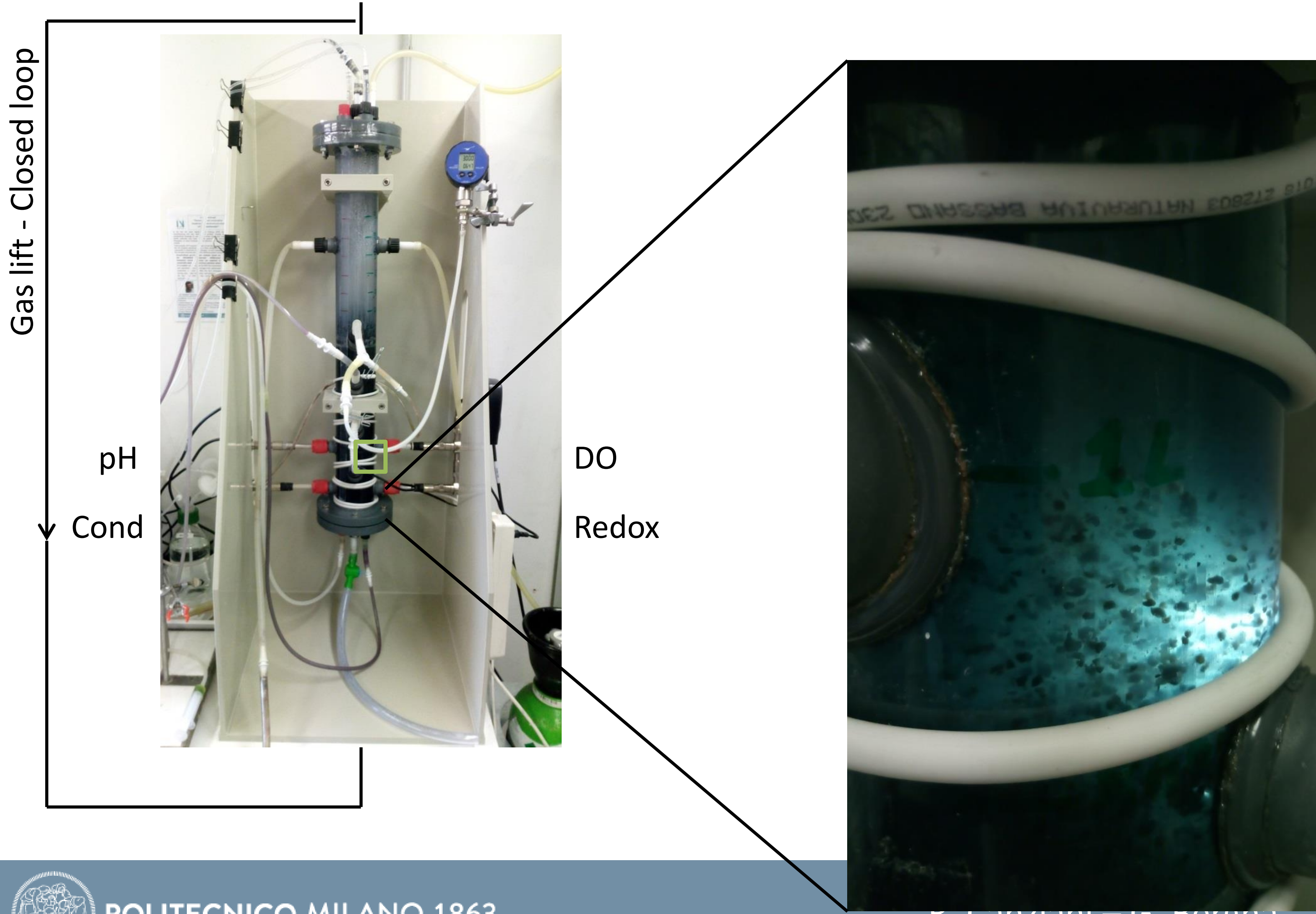
$$NH_4^+ + OH^- \longleftrightarrow NH_3 + H_2O$$

# Bench-scale pilot plant

- **Gas-lift SBR**
- **PLC control panel**
- Monitoring probes (DO, conductivity, ORP, pH)
- pH control (acid/base dosing)
- Heating for keeping constant T = 30±1ºC

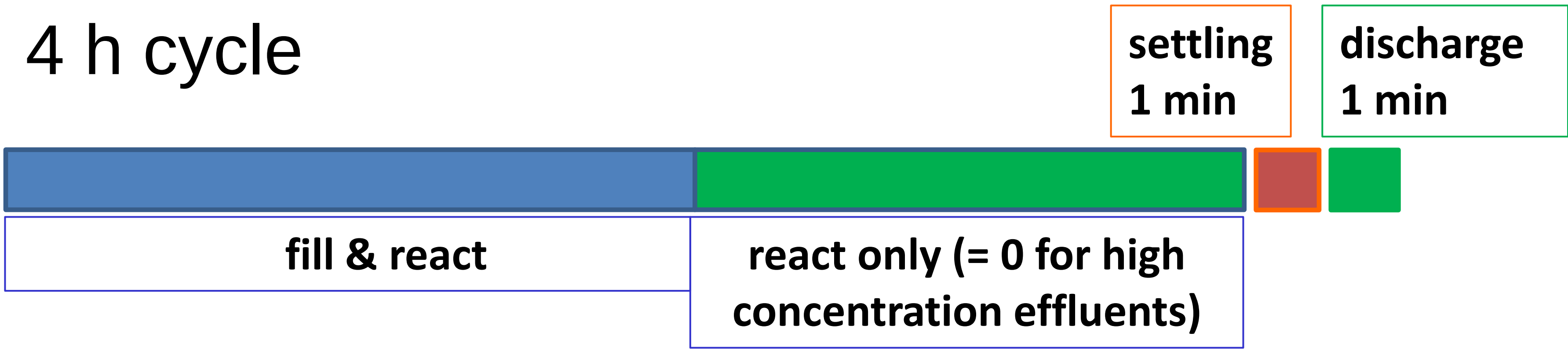


# Bench-scale pilot plant



# Bench-scale pilot plant results

- 4 h cycle



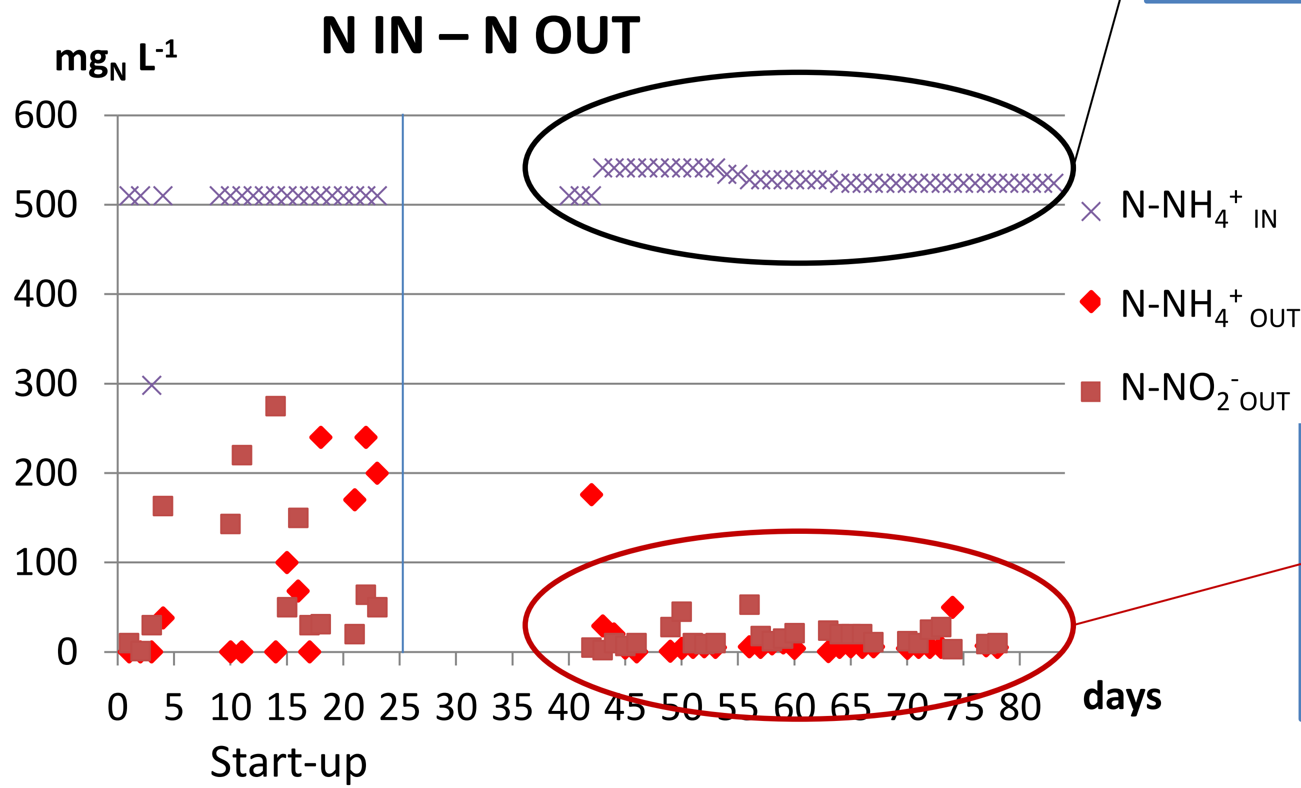

- *T = 31 - 32°C*
- *DO = 0,07 - 0,40 mg/L*
- *pH = 7,2 -7,5*

Biomass: **5 - 10 $g_{SSV}$/L**

# Bench-scale pilot plant results

## Equalized effluent (I)

**Influent**
**Ntot ≈ N-$NH_4^+$ = 520 $mg_N$/L**

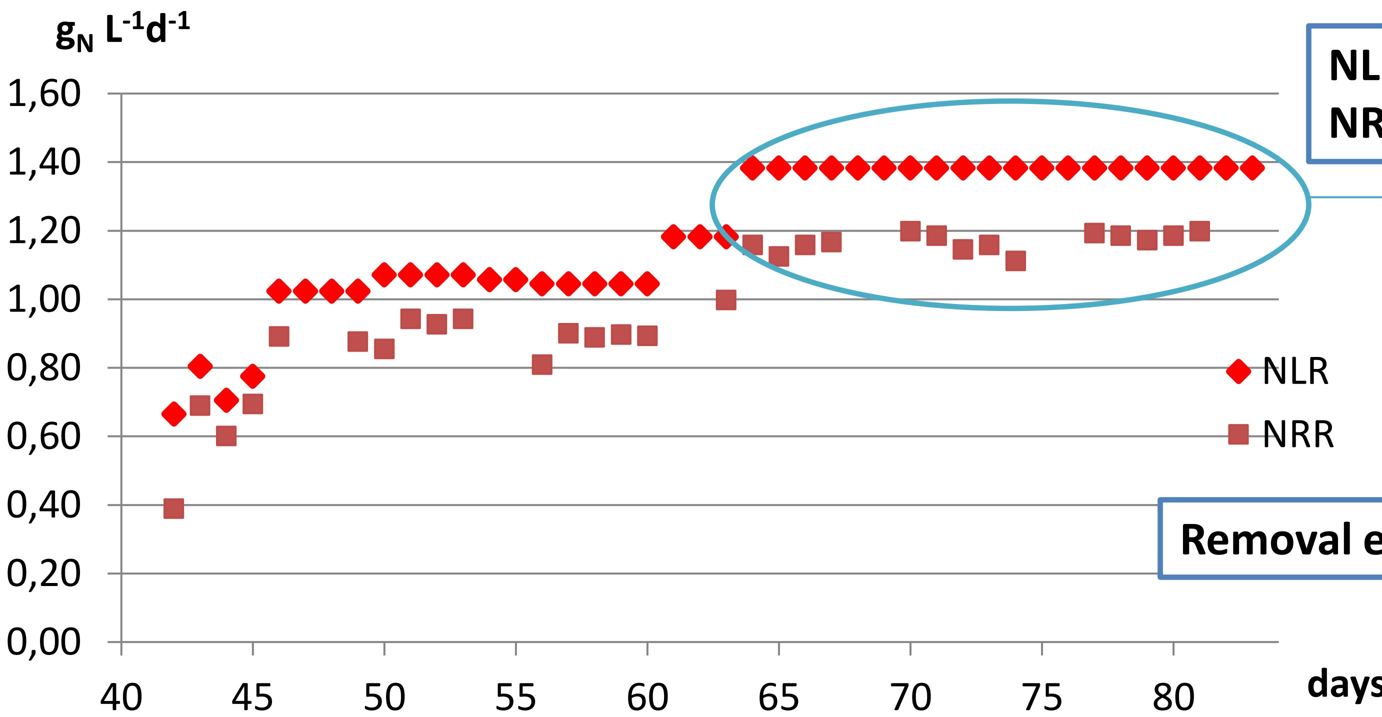



**Effluent**
**N-$NH_4^+$ = 8 $mg_N$/L**
**N-$NO_2^-$ = 16 $mg_N$/L**
**N-$NO_3^-$ = 55 $mg_N$/L**
**$N_{tot}$ = 79 $mg_N$/L**

# Bench-scale pilot plant results

## Equalized effluent (II)

Volumetric N Loading rate (**NLR**) and N removal rate (**NRR**)




**NLR = 1,38 $g_N\ L^{-1}\ d^{-1}$**
**NRR = 1,17 $g_N\ L^{-1}\ d^{-1}$**

**Removal efficiency = 85%**

# Application 1: testing real DTP effluents IN THE LAB

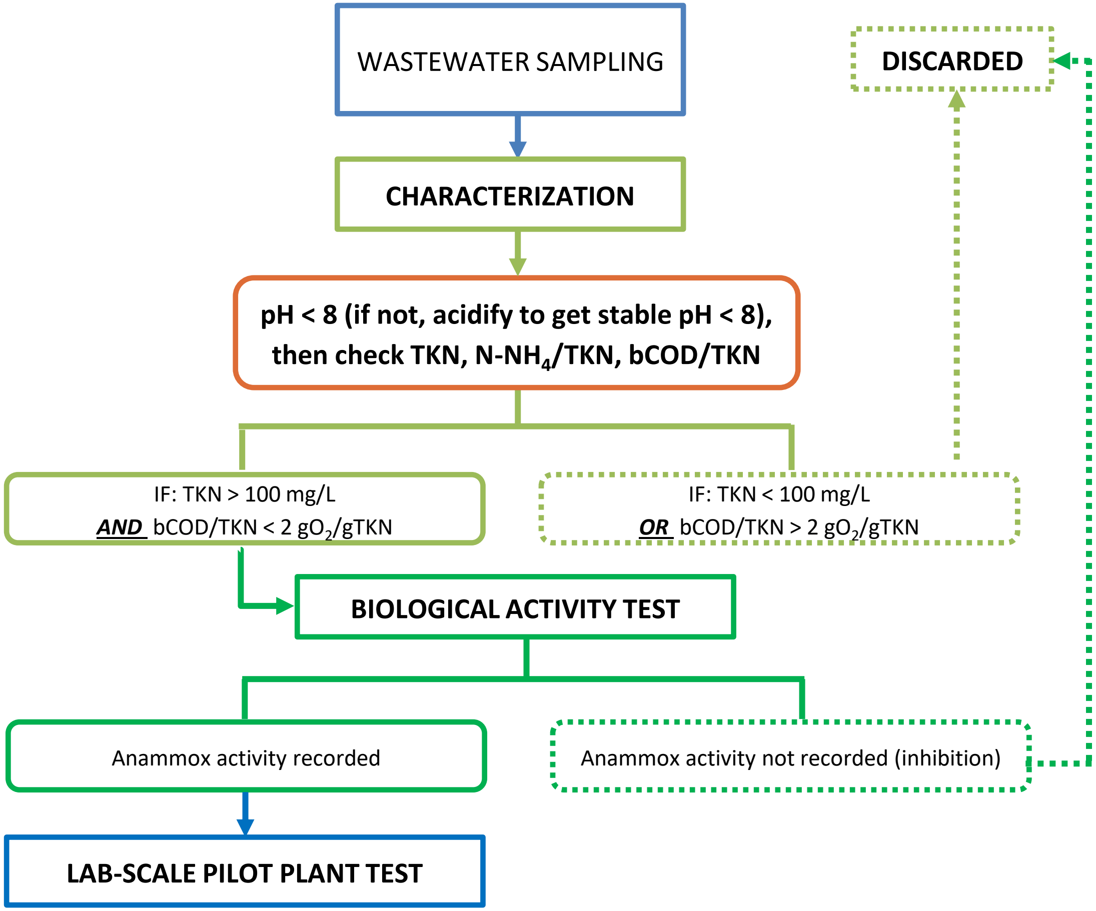
- Standardized method for testing Anammox biomass activity on specific wastewater
- Lab-scale pilot for longer testing (2-3 days), based on the Life DeNTreat technology,
- “portable clinic”:
  - ❖ testing heterogeneous wastewater samples
  - ❖ providing a rapid and reliable quotation for industrial-scale treatment plants

# Application 1: testing real DTP effluents IN THE LAB

An "if – then schema" has been developed to check if the wastewater can be treated by the PN/ Anammox process.

A sort of "Hardware Development Kit [HDK]" will be elaborated easing the reapplication of the LIFE DeNTreat experience to the widest application contexts possible.

Lariana and Polimi will support prospective adopters by  consultancy activity.



# Application 2: demonstration plant at a DTP factory

A TRL7 pre-industrial wastewater treatment plant operating in a representative operational environment processing up to 40 $m^3$/day of wastewater (8 kgN/d)

After the project the demo plant will be installed from time to time in the companies interested in adopting the new process, to get operational data and detailed specifications useful for the design and construction of full-scale plants.

Grazie per l’attenzione