# EOLI

The European Commission
Community Research
Confirming the International Role of Community Research

*Efficient Operation of Urban Wastewater Treatment Plants*

## Second Annual Meeting

## Milano, Italy

## 22th to 24th November 2004

# Work Package 1


POLITECNICO DI MILANO

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POLIMI

ENEA

# **Main** POLIMI activities in the second year

Operation of the lab-scale **SBR (POLIMI)** aimed to:

- Performing further 11 cyclic tests for model calibration (WP2) (see LLN presentation)
- Evaluating process abnormal conditions (WP6)
- Test potential applications of the off-line titrator (WP3) (more in WP3 presentation)

Setting up and operation of a pilot-scale **SBR (ENEA)** aimed to:

- Test the on-line titrator (WP3)
- Evaluate process abnormal conditions (WP6)

# Operation of the POLIMI SBR

Operated continuously except for:

stop 1: 22/12/03 – 14/01/04 (Christmas holidays)

stop 2: 22/07/04 – 10/09/04 (Summer holidays)

Loading conditions

- operating days 1- 380: synthetic influent
  COD = 600 mg/L; N = 75 mg TKN/L (COD/N = 8).
  VER = 0.2 Loading rate $C_{COD}$ = 9.6 gCOD/d.
- operating days 432 – onward: synthetic influent +acetate
  COD = 1320 mg/L; N = 150 mg TKN/L (COD/N = 8.8).
  VER = 0.3 Loading rate $C_{COD}$ = 21.1 gCOD/d.

# Operation of the POLIMI SBR

The SBR was operated in 4 cycles per day

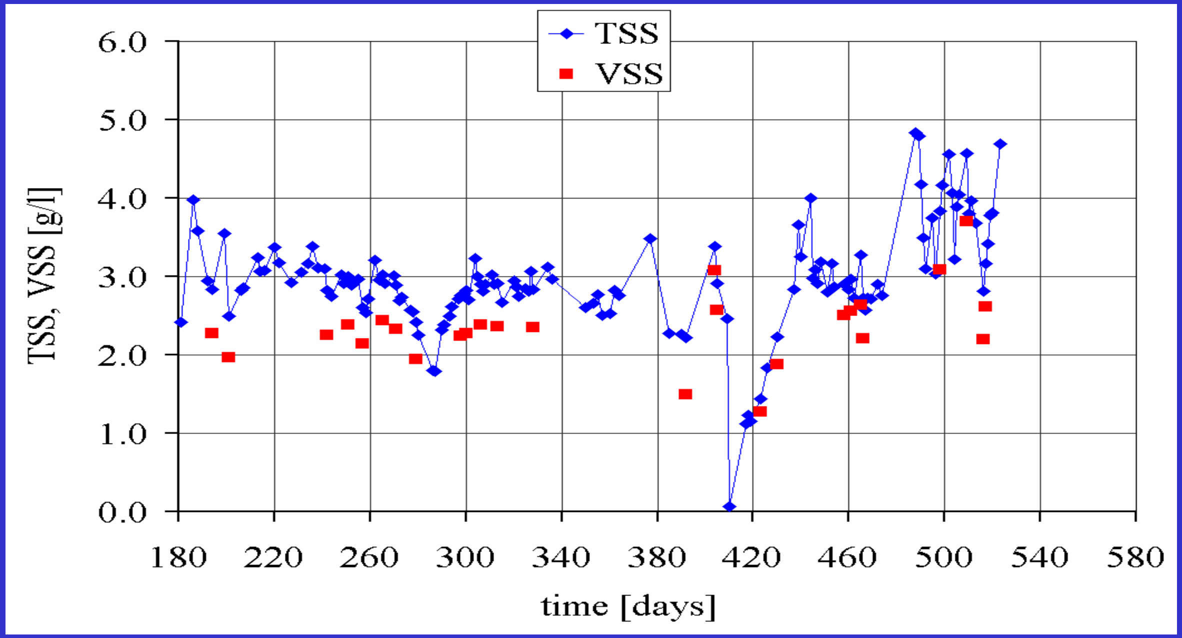
Each cycle included the following phases:

| | |
|---|---|
| ANOXIC FILL | duration $t_F$ = 10 min; |
| ANOXIC REACT | duration $t_{ANOX}$ → Varied; |
| AEROBIC REACT | duration $t_{AER}$ → Varied; |
| SETTLE | duration $t_S$ = 37 min; |
| DRAW | duration $t_D$ = 23 min; |

| | |
|---|---|
| operating days 1- 207: | $t_{ANOX}$ = 2.5 h, $t_{AER}$ = 2.5 h; |
| operating days 208- 235: | $t_{ANOX}$ = 2.0 h, $t_{AER}$ = 3.0 h; |
| operating days 236-465: | $t_{ANOX}$ = 1.5 h, $t_{AER}$ = 3.5 h; |
| operating days 466- onward: | $t_{ANOX}$ = 1.0 h, $t_{AER}$ = 4.0 h; |

# Operation of the POLIMI SBR

Biomass



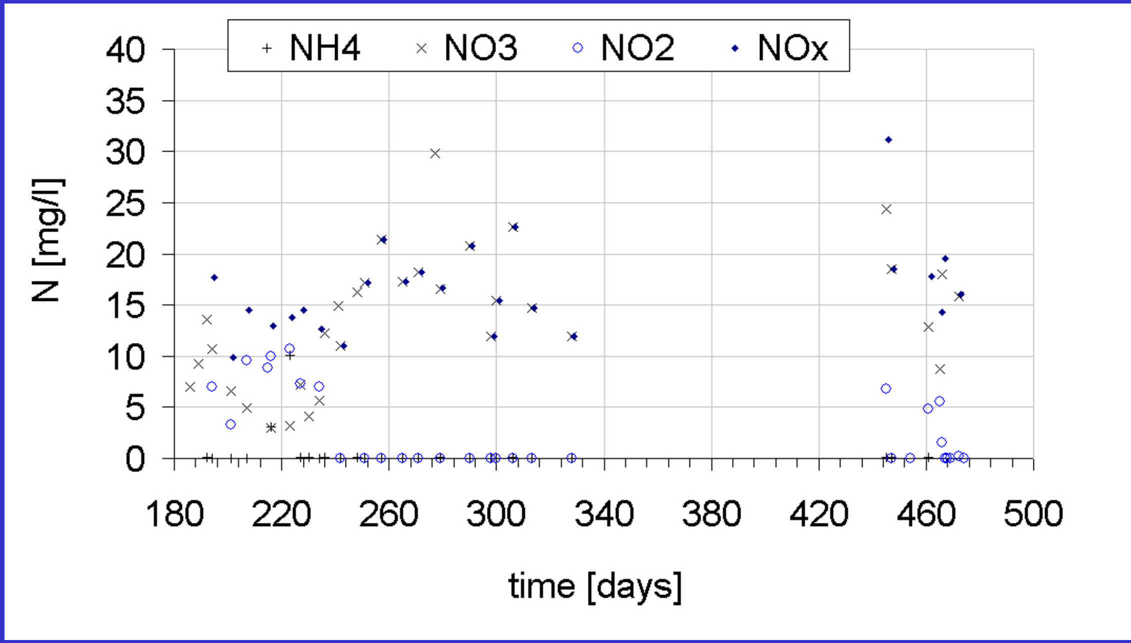

*Up to day 410*: TSS around 3 g/L. SRT ≈ 27 d.

*day 410-432*: sludge loss → no biomass wastage during the following month.

*day 432 onward*: VSS around 4.5 gTSS/L. SRT ≈ 9-11 d (instable nitrification)

# Operation of the POLIMI SBR

N forms




Ammonium oxidation: Normally satisfying. Recently loss of nitrification capacity was deduced from DO/pH trends.

Nitrites built up

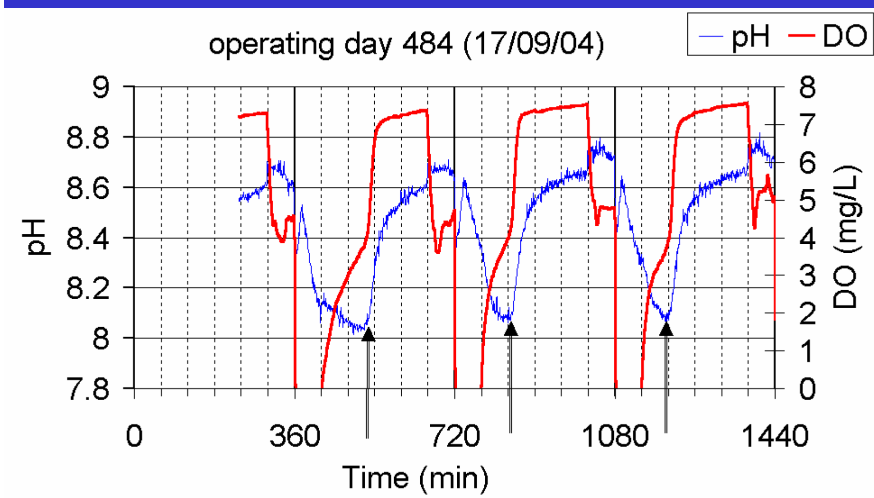
Nitrates increased as a consequence of $t_{anox}\downarrow$ & $t_{aer}\uparrow$

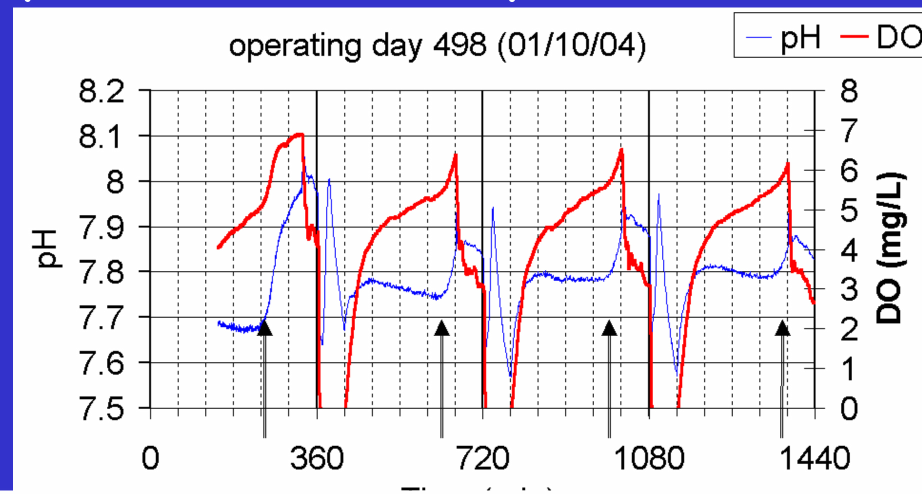
(and unfavorable COD/N)

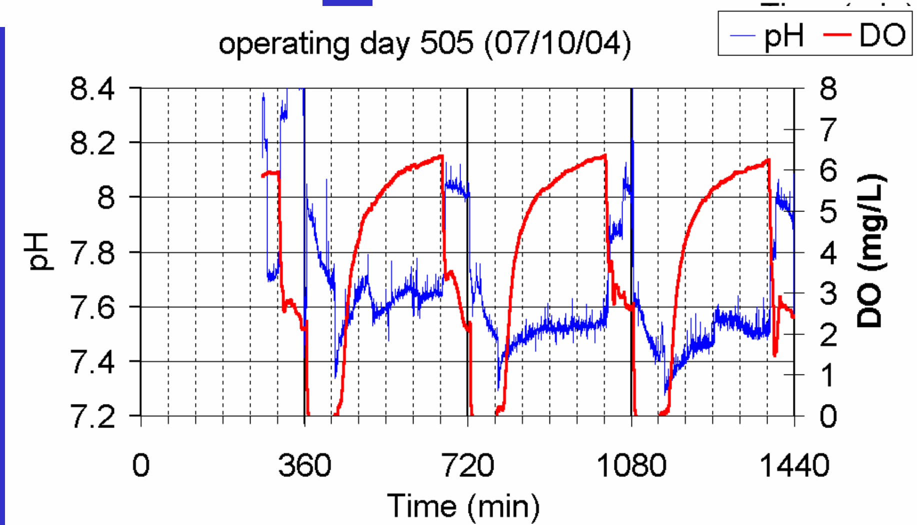
# Operation of the POLIMI SBR

## N forms

### Loss of nitrification capacity deduced from pH/DO trends



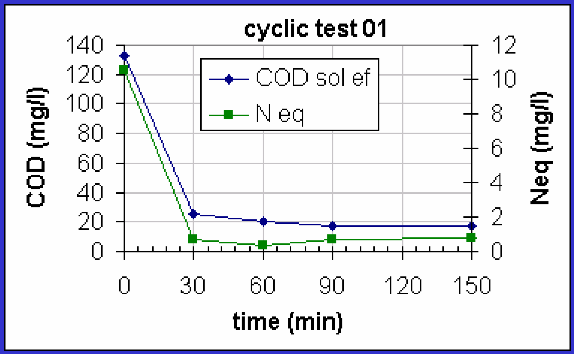



# Operation of the POLIMI SBR

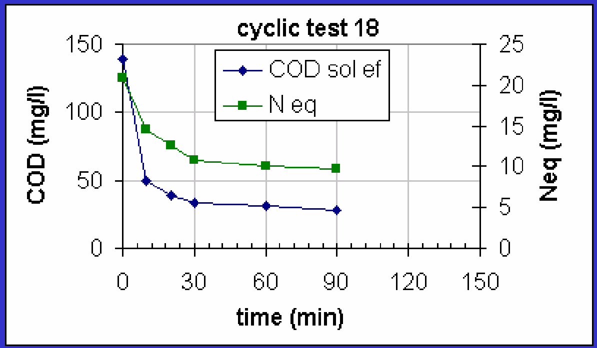
## N forms

Denitrification efficiency




Excessively long anoxic phase

Sufficient COD for N reduction




Shortened Anoxic phase

Insufficient COD for N reduction

(more NOx available from longer aeration phase)

# Abnormal conditions

## Reduced nitratation capacity

Episode 1: (Already reported). It happened after SBR start up. Ammonium oxidation was ok. Nitratation could not be restored, new sludge had to be seeded.

*Hypothesis:* nitrite oxidisers had not recovered from long storage in the refrigerator.

Consistent with Grunditz and Dalhammar *(2001)*: under storage conditions (3°C in liquid medium):

kd(*Nitrobacter*) > kd(*Nitrosomonas)*

Also Morgenroth et al., 2000: during long (weeks) idle periods in SBR

kd(*NOB*) > kd(*AOB)* → nitrites accumulation after re-start

*Operational consequence:* long anoxic periods can imbalance nitrification capacity

# Abnormal conditions

## Reduced nitratation capacity

Episode 2:

*Cause:* 10 Jun: the SBR load was doubled
19/20 Jun: 8 anoxic cycles

Nitrites ↑ to 6.8 mgN/L (22 Jun )

*Action:* feeding was stopped, aeration was kept on (21/22 Jun ).

24 Jun : Nitrites were 0.02 mgN/L

Episode 3:

*Cause:* 29 Jun: 3 anoxic cycles

Nitrites ↑ to 4.9 mgN/L (8 Jul ), 5.6 mgN/L (12 Jul ),

*Action*: feeding was stopped and aeration was kept on 12/13 Jul

14 Jul : Nitrites were 0.02 mgN/L

# Abnormal conditions

## Reduced nitratation capacity

Episode 2 and 3 were generated by transient unfavourable conditions (prolonged anoxic conditions under high loading rate).

Nitratation could be restored.

Operating strategy:

prolonged anoxic conditions are to be avoided

Low $t_{AER}/t_{ANOX}$ can favour nitrite built up

*Rhee et al. (1997) observed that in SBR with nitrite build-up, aerobic phases were always shorter than 4 hours.*

# Reduced nitratation capacity

## In the literature Environmental factors influencing nitrite build up:

### **pH**

Optimal range: (*Alleman, 1984*):

AOB = 7.9 – 8.2

NOB = 7.2-7.6

High pH values (>7.8) favour nitrite build up:

in nitrification (*Merkel et al., 1993; Schuch et al., 2000*)

in denitrification (*Glass and Silverstein, 1998*)

Low pH values (<7.4) favour nitrite build up in denitrification

(in a granular trickling filter *Furumai et al.,1996*)

# Reduced nitratation capacity

**In the literature** Environmental factors influencing nitrite build up:

pH and Free ammonia (FA)

Free ammonia is known to inhibit NOB
(*Yang e Alleman, 1992; Anthonisen et al., 1976; Mauret et al., 1996*).

The ratio FA/(Total reduced nitrogen) increases with pH:

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

NOB inhibited for [N-$NH_3$] > 6.6 mg/L (*Mauret et al. 1996)*

Also FA/NOB mass ratio seems to be relevant (*Sutherson & Ganczarczyk, 1986*)

Inhibition threshold 0.5 – 3mgN-$NH_3$/mgNOB (*Rols et al., 1994*).

# Reduced nitratation capacity

## In the literature Environmental factors influencing nitrite build up:

### **Temperature**

Different effect of temperature on AOB and NOB growth rate:

$T_{opt}$NITRITATION > $T_{opt}$NITRATATION (*Wortman e Wheaton, 1991*)

$\mu$ NOB >> $\mu$ AOB    $10°C < t < 20°C$

$\mu$ NOB = $\mu$ AOB    $25°C < t < 30°C$

Temperature affects $NH_3/NH_4^+$ equilibrium: when T ↑, free ammonia↑ (NOB inhibitor) (*Mauret et al. 1996*).

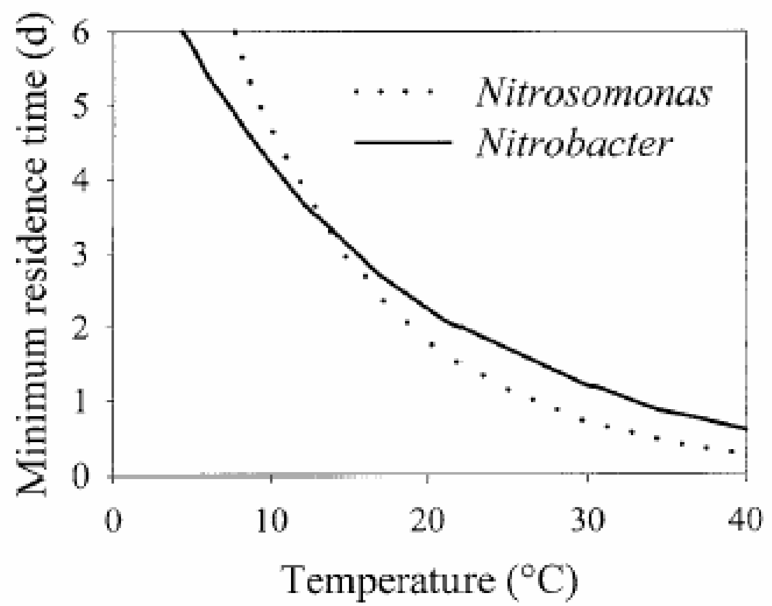



*Figure 4.* Effect of temperature on the minimal required cell residence time for ammonia and nitrite oxidation. Above 14 °C it is possible to wash out the NOB while maintaining the AOB (after Jetten et al. 1997, with temperature coefficients of Hunik et al. 1994).

$$SRT = 1/(\mu\text{-}kd)$$

# Reduced nitratation capacity

## In the literature Environmental factors influencing nitrite build up:

**Dissolved Oxygen - 1**

DO semisaturation constant is higher for NOB (*Hendrikus & Saskia, 1993; Barnes & Bliss,1983*):

$Ks_{,DO}$ (AOB) = 0.25-0.5 mg/L

$Ks_{,DO}$ (NOB) = 0.34-2.5 mg/L

*Hanaki et al (1990b)*: for DO<0.5:

AOB growth rate doubles

NOB growth rate does not vary sensibly

In a biofilm reactor a $O_2/NH_4^+$ mass ratio < 5 led to nitrites build up (*Ceçen & Gonenç, 1995*)

# Reduced nitratation capacity

## In the literature Environmental factors influencing nitrite build up:

### Dissolved Oxygen - 2

A sudden stop in the aeration system causes an immediate nitrite build up (*Laanbroek et al.,1994; Dancong et al., 2000)*

Nitrites build up was found to be proportional to the decrease in the aerobic period *Sung-Keun Rhee et al. (1997)* .

**In conclusion: NOB are less competitive at low DO levels.**

In denitrification:

DO inhibits nitrite reduction more than nitrate reduction.

Low DO concentrations in denitrification can lead to nitrite build up

Temporary nitrite built up in the beginning of the anoxic phase (*Krul & Veeningen 1977*)

# Reduced nitratation capacity

## In the literature Environmental factors influencing nitrite build up:

### Phosphorus

*Nitrification:* P semisaturation constant is higher for NOB (*Nowak et al. 1996*):

$Ks_P$ (AOB) = 0.03 mg/L

$Ks_P$ (NOB) = 0.2 mg/L

*Denitrification*: nitrite reduction is depressed in the presence of phosphate causing nitrites accumulation (Barak & van Rijn, 2000)

### Organic Matter

*Nitrification*: by increasing C/N, NOB activity was retarded (*Okabe et al. 1996*)

*Denitrification*: nitrite build up is favoured by:

- Using glucose as carbon source (*Wilderer et al.,1987*)
- Under organic carbon limiting conditions (Martienssen e Schops,1997).

# Abnormal conditions

## Loss in Nitrification capacity

This AC was recently observed

Evidence: effluent ammonium built up
modified pH and DO trend during AER REACT

Cause: probably due to excessive sludge wastage after load increase and consequent Nitrifiers wash out (although sludge age was around 9-11 days).

Action: reduction of sludge wastage and loading rate.
Very slow recovery was observed.

# *Batch experiments for further characterization of the denitrification process*

Tests performed in batch at various loading conditions to evaluate the feasibility to monitor the denitrification process by pH-stat titration (WP3).

| **Test number** | **N form** | **Loading condition ($mL_{synthetic\ influent}/L_{sludge}$)** | **SSV (g/L)** | **T (°C)** | **pH** |
|---|---|---|---|---|---|
| 1 | $NO^-_3$ | 20 | 3.2 | 23.5 | 7.6 |
| 2 | $NO^-_3$ | 20 | 2.7 | 24 | 7.5 |
| 3 | $NO^-_3$ | 20 | 2.7 | 23 | 7.5 |
| 4 | $NO^-_3$ | 20 | 2.5 | 24 | 7.7 |
| 5 | $NO^-_3$ | 30 | 2.5 | 24 | 8.0 |
| 6 | $NO^-_3$ | 30 | 2.6 | 24 | 7.9 |
| 7 | $NO^-_3$ | 40 | 2.3 | 23 | 7.6 |
| 8 | $NO^-_3$ | 40 | 2.4 | 24 | 7.7 |
| 9 | $NO^-_2$ | 20 | 3.1 | 24 | 7.85 |
| 10 | $NO^-_2$ | 20 | 2.9 | 25 | 7.9 |
| 11 | $NO^-_2$ | 30 | 3.2 | 25 | 7.8 |
| 12 | $NO^-_2$ | 40 | 2.4 | 25 | 7.9 |
| 13 | $NO^-_2$ | 40 | 2.6 | 25 | 7.8 |

## *Batch experiments for further characterization of the denitrification process*

Results indicated that nitrite reduction rate was faster in tests were nitrites where the only electron acceptor than in tests were nitrates were dosed.

| | Max rate (mgN/mgSSV h) | |
|---|---|---|
| | Tests on $NO_2^-$ | Tests on $NO_3^-$ |
| Nitrate reduction | | 6.8 |
| Nitrite reduction | 5.7 | 4.8 |

Results on pH-stat titration will be presented in the WP3 section.

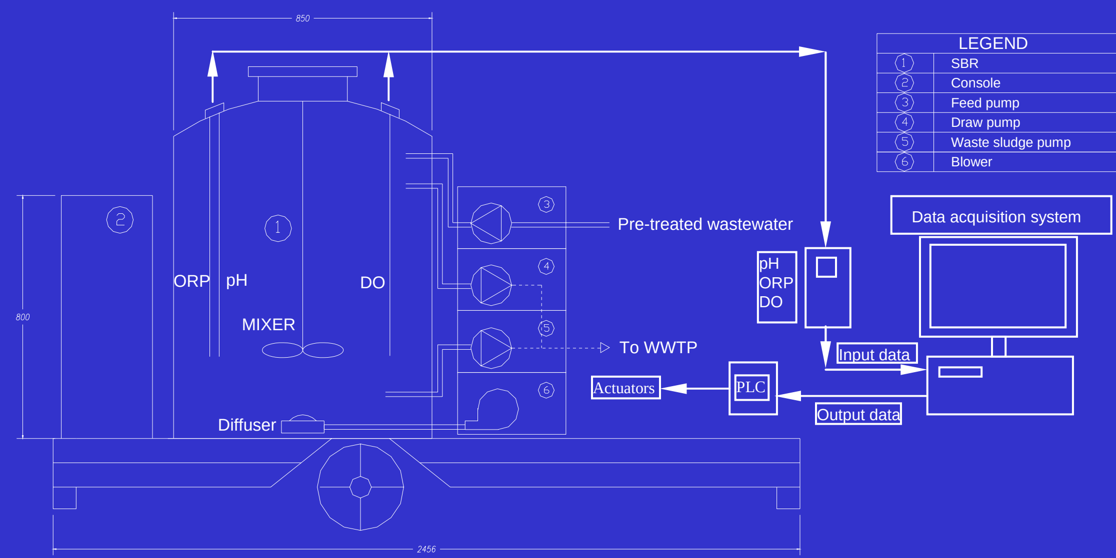
# Operation of the ENEA pilot SBR

- SBR located side stream to a municipal WWTP
- fed on real sewage drawn after grit removal
- Operated continuously from 31/05/04 except for:
  - 6th – 16th August (Summer holidays)

Influent main characteristics during peak load (9-10 AM working days)

| parameter | mean value |
|---|---|
| CODtot [mg/L] | 471 |
| CODsol [mg/L] | 302 |
| CODsol/CODtot [g/g] | 66% |
| TKN [mg/L] | 59 |
| $N\text{-}NH_4^+$ [mg/L] | 52.4 |
| CODtot/TKN [g/g] | 8.2 |
| $N\text{-}NH_4^+$ /TKN [g/g] | 88% |
| TSS [g/L] | 0.18 |
| VSS [g/L] | 0.08 |
| pH | 7.5 |

# Pilot plant Layout



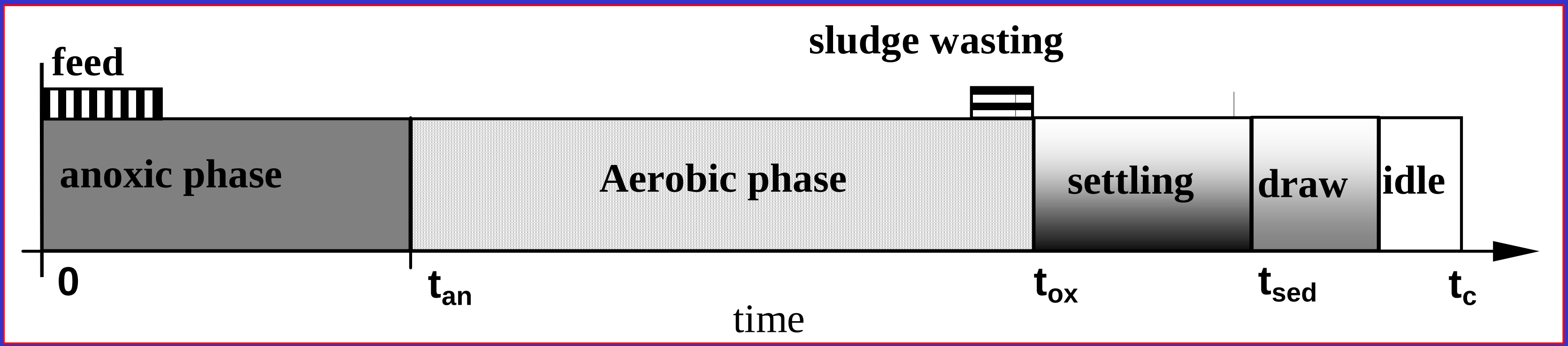

working volume 500 L

equipment:

- mechanical mixer
- variable-flow blower connected to membrane diffuser
- two peristaltic pumps for influent loading and effluent discharge
- pump for sludge wastage
- multi-parameters converter for on-line acquisition of pH, DO, ORP, T
- signals recorded by multi-function data acquisition card, installed on PC
- software application developed in LabView 6.1 (National Instruments) to manage data acquisition
- Actuators controlled by a PLC interfaced to the acquisition card

# Operation of the ENEA pilot SBR

- the SBR was operated in 4 cycles per day
- total cycle duration 6 h
- Each cycle included the following phases:



# Operation of the ENEA pilot SBR

## Phases duration from 31st May to 6th August 2004

| | |
|---|---|
| ANOXIC FILL | duration $t_F$ = 17 min; |
| ANOXIC REACT | duration: $t_{ANOX}$ = 1.5 h; (FILL included) |
| AEROBIC REACT | duration $t_{AER}$ = 2.5 h; |
| SETTLE | duration $t_S$ = 40 |
| DRAW | duration $t_D$ = 17 |
| IDLE | duration $t_I$ = 63 min |

fast denitrification (30 min maximum)
good nitrification rates

## Phases duration from 16th August to 28th September 2004

| | |
|---|---|
| ANOXIC FILL | duration $t_F$ = 19 min; |
| ANOXIC REACT | duration: $t_{ANOX}$ = 1 h; (FILL included) |
| AEROBIC REACT | duration $t_{AER}$ = 3 h; |
| SETTLE | duration $t_S$ = 40 min; |
| DRAW | duration $t_D$ = 19 min; |
| IDLE | duration $t_I$ = 61 min |

decreased anoxic phase duration and increased aerobic phase to improve nitrification capacity because of high influent ammonia concentration

# Operation of the ENEA pilot SBR

Effect of phase duration changes on the process: slight increase in nitrate effluent content (because of incomplete denitrification during anoxic phase)

However, total nitrification not always achieved with peak load cycles (SBR loading at 10 am)

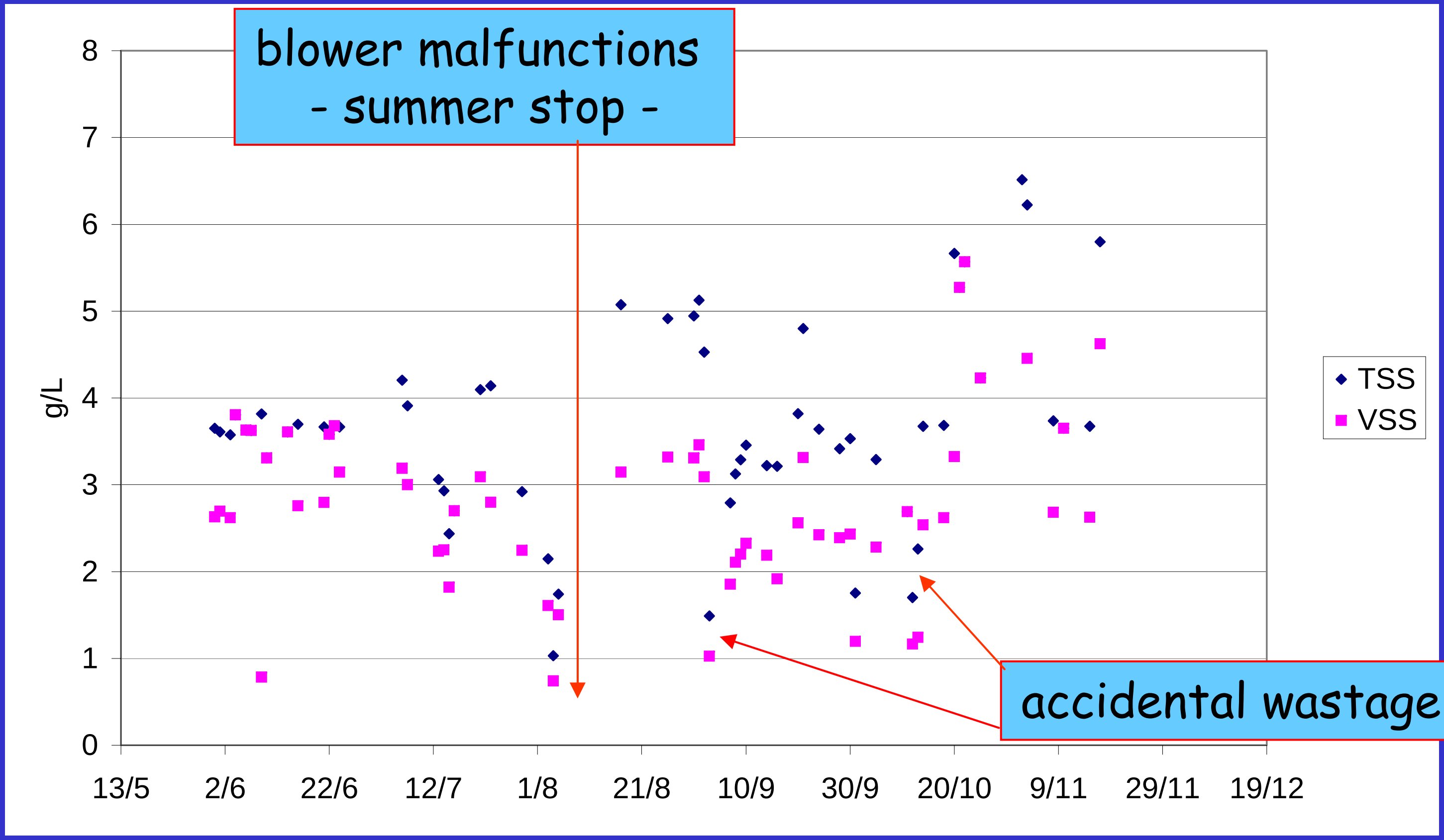
## Phases duration from 28th September onward

| | |
|---|---|
| ANOXIC FILL | duration $t_F$ = 19 min $\rightarrow$30 min (fill volume=150L); |
| ANOXIC REACT | duration: $t_{ANOX}$ = 1.5 h $\rightarrow$1h 20 min; (FILL included) |
| AEROBIC REACT | duration $t_{AER}$ = 3.5 h $\rightarrow$3h 20 min; |
| SETTLE | duration $t_S$ = 40 min; |
| DRAW | duration $t_D$ = 19 min $\rightarrow$ 30 min (fill volume=150L); |
| IDLE | duration $t_I$ = 10 min |

anoxic phase and aerobic phase duration increased

# Operation of the ENEA pilot SBR

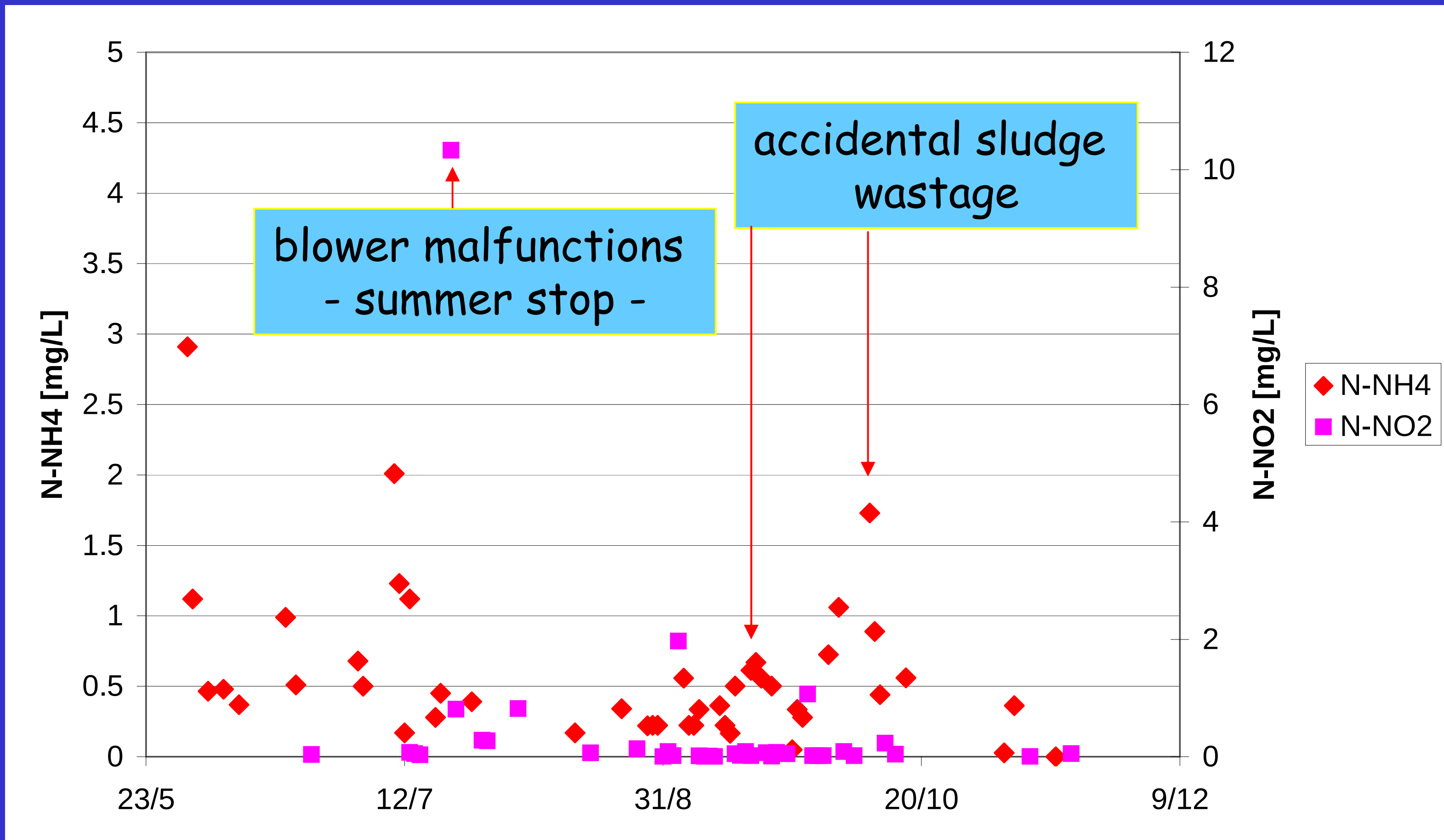
## Biomass: TSS and VSS trends




- Sludge purge operated to keep SRT = 21 days
- Last month: reduced sludge purge to provide sludge for On-Line titrator tests (see WP3 POLIMI report)

# Operation of the ENEA pilot SBR

N forms: N-$NH_4$ and $NO_2$ trends in SBR effluent of the early morning cycle (sewage load at 4 AM)



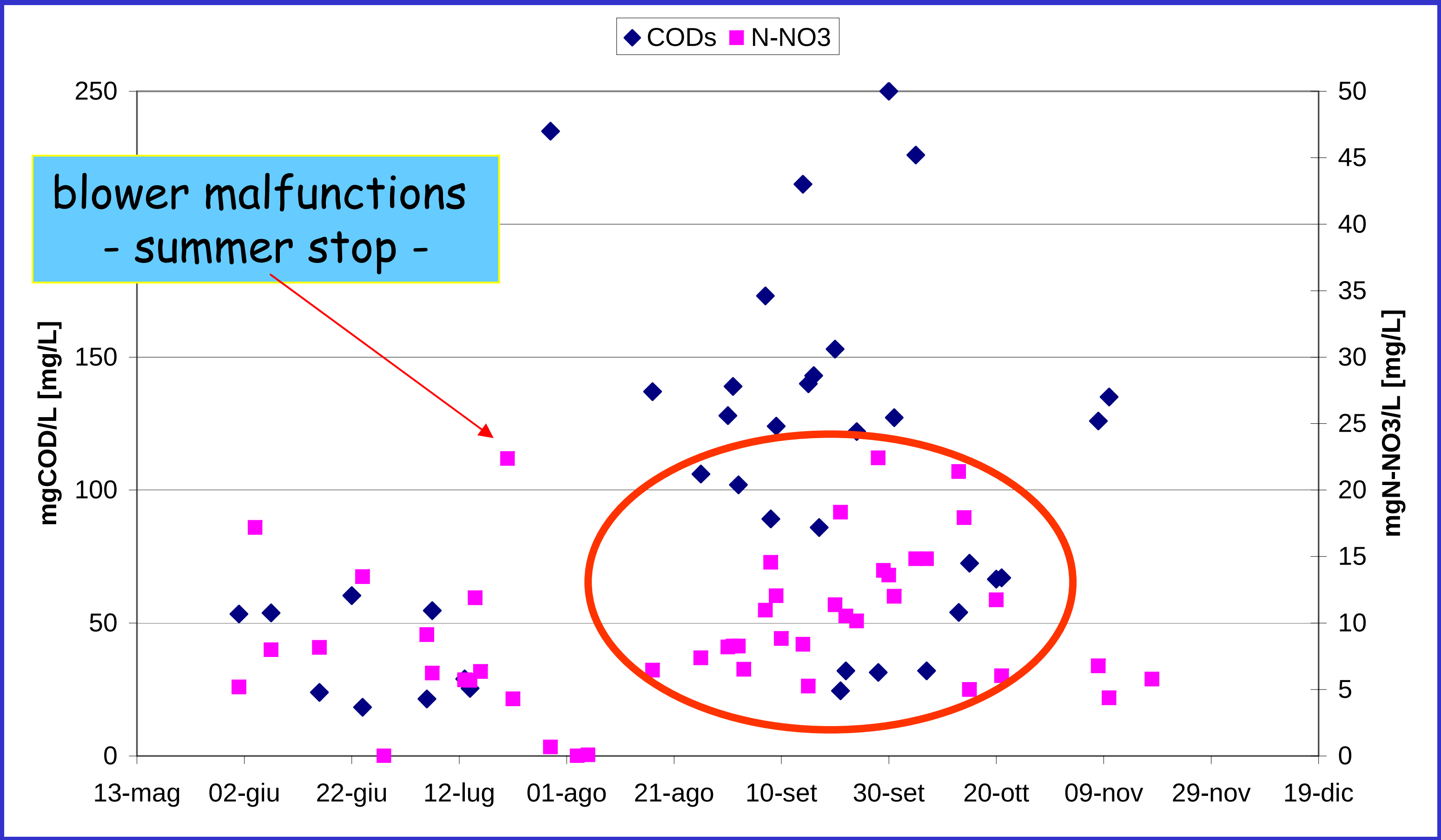

Ammonium oxidation: normally satisfying

NO Nitrites build up

# Operation of the ENEA pilot SBR

COD and $NO_3$ trends in SBR effluent of the early morning cycle

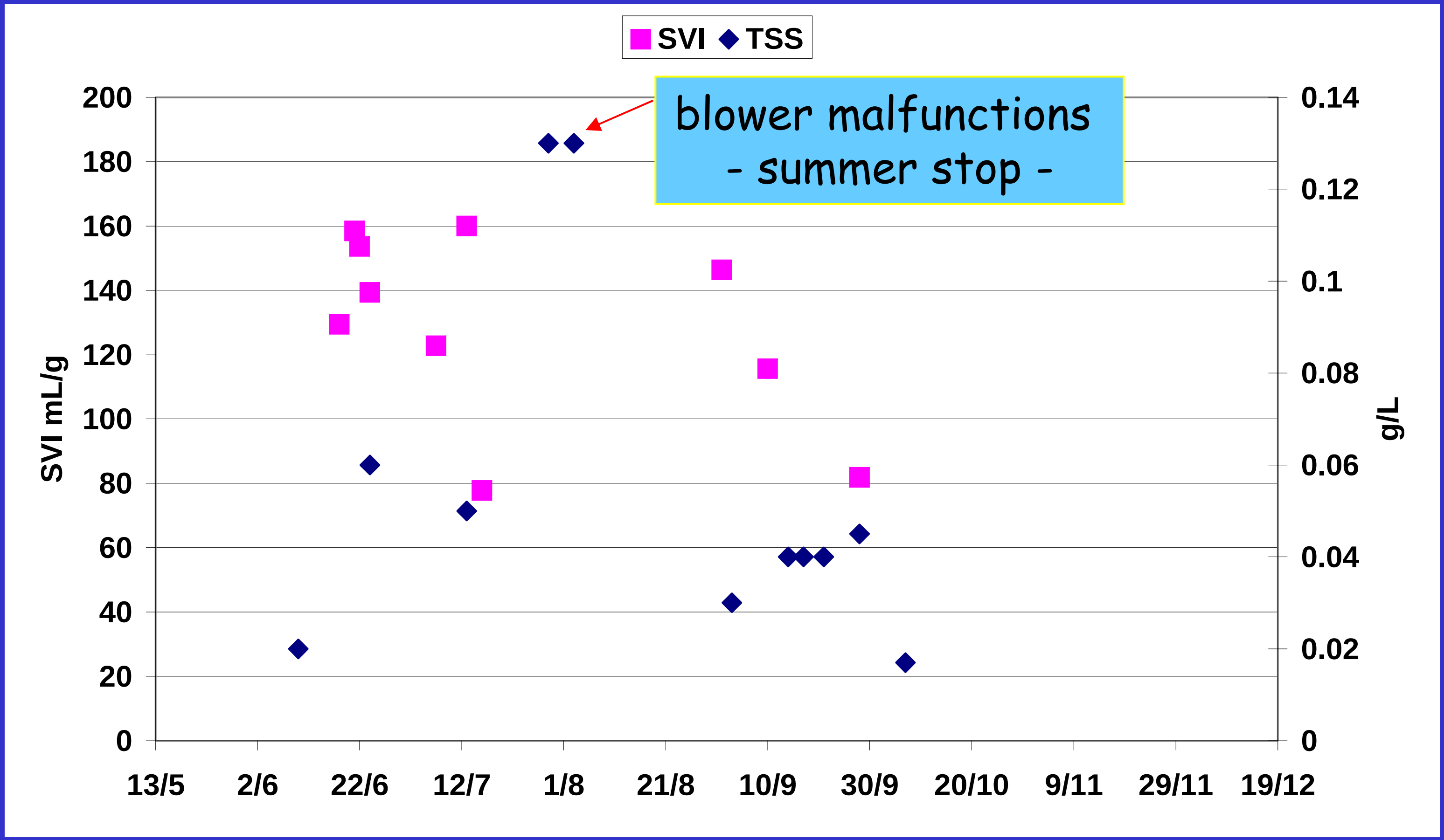
(FILL at 4 AM)




Nitrates increased as a consequence of $t_{anox}\downarrow$ and unfavorable COD/N $\rightarrow$ COD removal not always satisfying

# Operation of the ENEA pilot SBR

## Effluent TSS and SVI

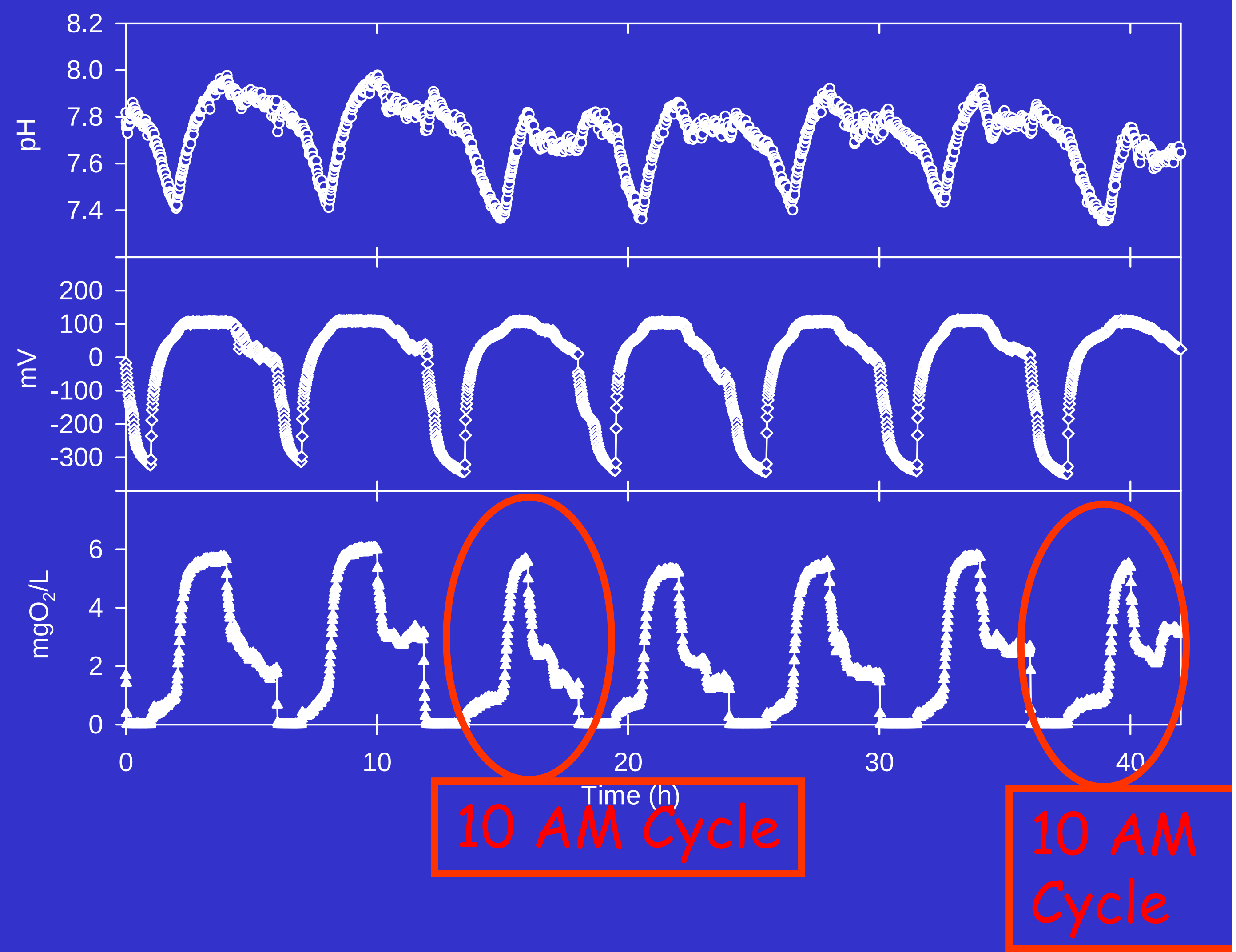



Sufficiently good settleability of the sludge during the whole experimental period

# Operation of the ENEA SBR

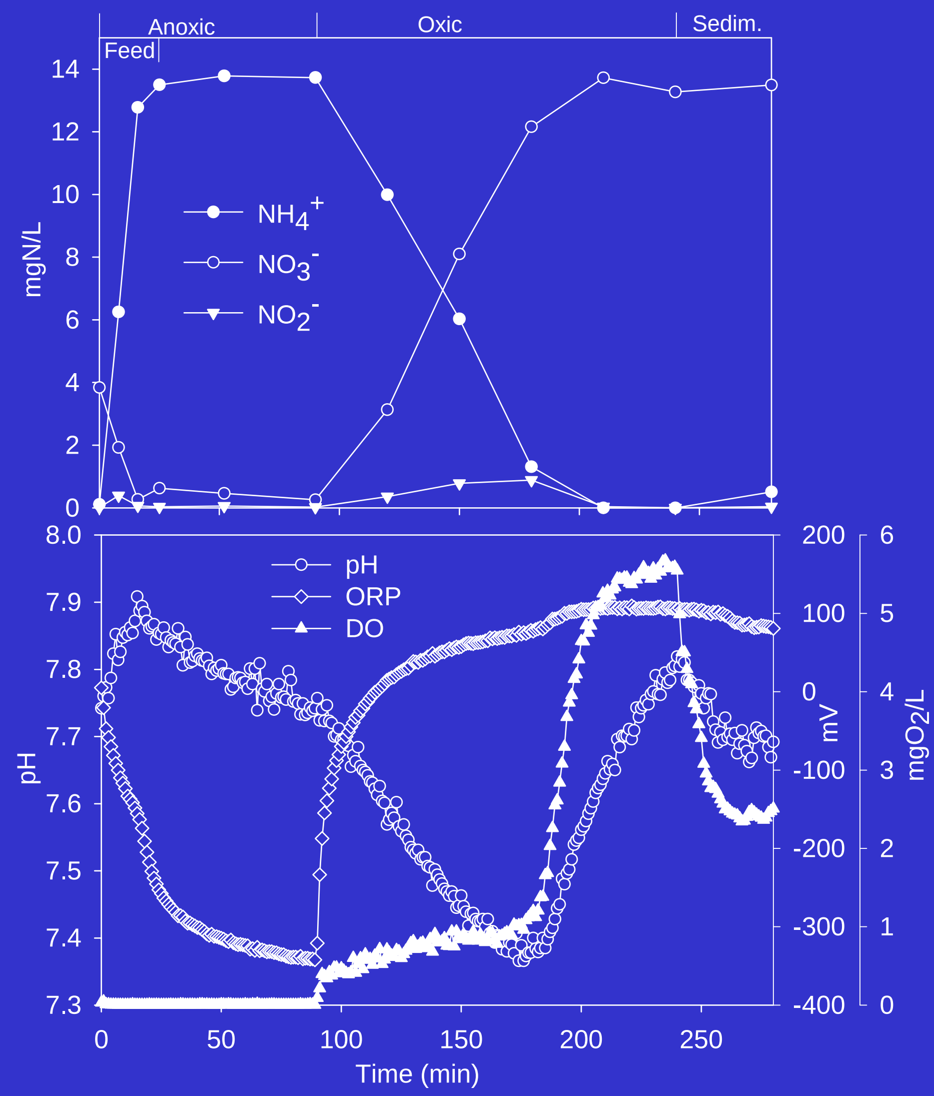
- Examples of continuous on line acquisition of pH, ORP, DO.

- Graph show seven consecutive cycles



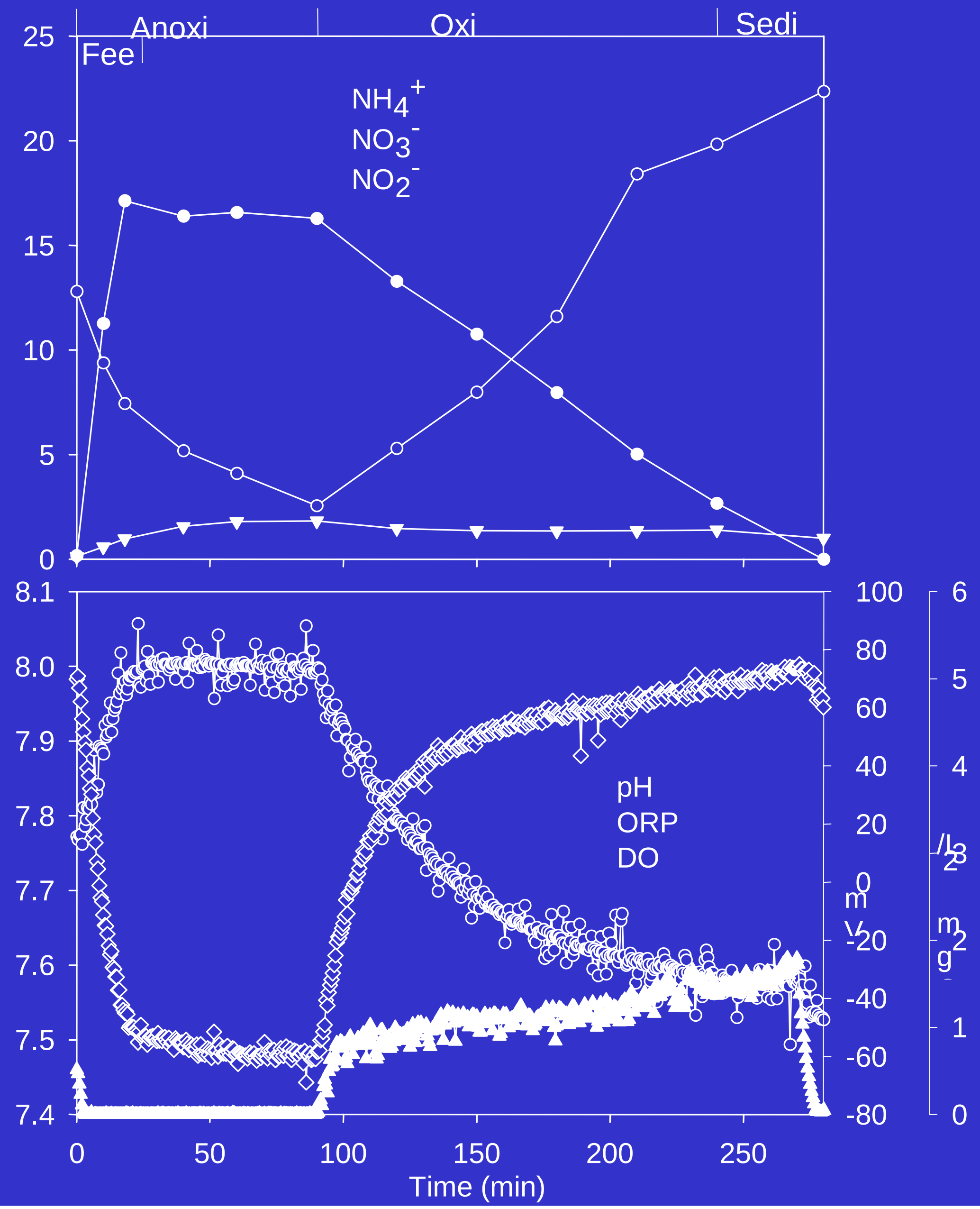
# Operation of the ENEA SBR

- Cyclic test 24-06-04
  - ✓ Denitrification and nitrification processes are completed
  - ✓ The end of biological processes is obvious from the trend of pH, ORP, DO



# Operation of the ENEA SBR

- Cyclic test 28-09-04
  - ✓ Denitrification process is not completed
  - ✓ Nitrification process not completed (not adequate duration of aerobic phase)
  - ✓ Oxidation of nitrites is not completed



# Operation of the ENEA SBR

- Cyclic test 7-10-04
  - ✓ Denitrification process not completed, with accumulation of nitrates and nitrites at the end of anoxic phase
  - ✓ Nitrification process completed just after 3.5 h oxidation
  - ✓ After this test, increase of the fill volume up to 150 liters

# Abnormal conditions

## *Incomplete denitrification during anoxic phase and effluent nitrates build up*

causes:

- low COD/N ratio = 8.2 (8 is reported as the lowest threshold value)
- COD quality changes (sometimes low biodegradable COD fraction)

Respirometric tests performed by MARTINA titrator (see WP3 POLIMI report) attesting average **ratio rbCOD /COD = 10%**

- 10% ratio reported to cause denitrification problems (Tasli et al., 1999)

Influent characterization

performed from October 12th to October 21st

Samples withdrawn between 9:00 and 10:00 a.m. (peak load)

| PARAMETER | (mg/l) | ST.DEV. | METHOD |
|---|---|---|---|
| $COD_T$ | 250-400 | - | APHA 1992 |
| $COD_S$ | 200-350 | - | APHA 1992 |
| pH | 8.1 | 0.07 | Potentiometric |
| TSS | 135 | 0.02 | APHA 1992 |
| VSS | 30 | 0.01 | APHA 1992 |
| $N\text{-}NH_4$ titration | 51.8 | 10.7 | APHA 1992 |
| $N\text{-}NH_4$ spectrophotometer | 65.4 | 6.8 | APHA 1992 |
| TKN | 69.8 | 4.5 | APHA 1992 |
| BOD/COD | 0.4-0.7 | - | APHA 1992 |

# Abnormal conditions

***Incomplete denitrification during anoxic phase and effluent nitrates build up***

Corrective actions performed:

- increased anoxic reaction phase duration
- increased volumetric exchange ratio from 20 to 30%
  (Fill volume from 100L to 150L)

Denitrification potential estimated as suggested by Metcalf & Eddy (2003) to verify the opportunity to increase influent load without aversely affecting nitrification efficiency

# Future activities

POLIMI SBR

… to be agreed according to other WPs needs

Ideas:

Further insight in factors affecting nitrite build-up: the influence of pH and ORP on nitrite oxidation activity will be investigated experimentally.

Adsorption experiments will be carried out to be compared to Narbonne results

# Future activities

ENEA SBR

On-Line process monitoring (nitrification-denitrification) by means of the TITration Automatic ANalyzer

perform 24h influent characterization by means of an auto-sampler

… to be agreed according to other WPs needs

Ideas:

Observing abnormal conditions (nitrates and nitrites build-up, artificially induced by stressing the process)