

# 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

### 22<sup>th</sup> to 25<sup>th</sup> November 2004

## Work Package 3



**POLITECNICO  
DI MILANO**

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## POLIMI

## ENEA

## POLIMI/ENEA +SPES Objectives

1. Evaluate an existing lab-scale titration (DO-stat and pH-stat) sensor to monitor the performance of an SBR
2. Develop an automated combined pH-DO stat titration unit to be used for on-line SBR monitoring

## SUMMARY

1. Further insights on the applicability of pH/DOstat titration to monitor the nitrification processb (LLN)
2. pH/DOstat titration tests on sludge and sewage samples from a full scale WWTP
3. pH-stat denitrification tests on SBR influent
4. Development of the on-line pH/DO-stat titrator
5. Conclusions & future activities

## pH-stat denitrification tests on SBR influent

13 Batch tests by adding SBR influent + nitrites &/or nitrates

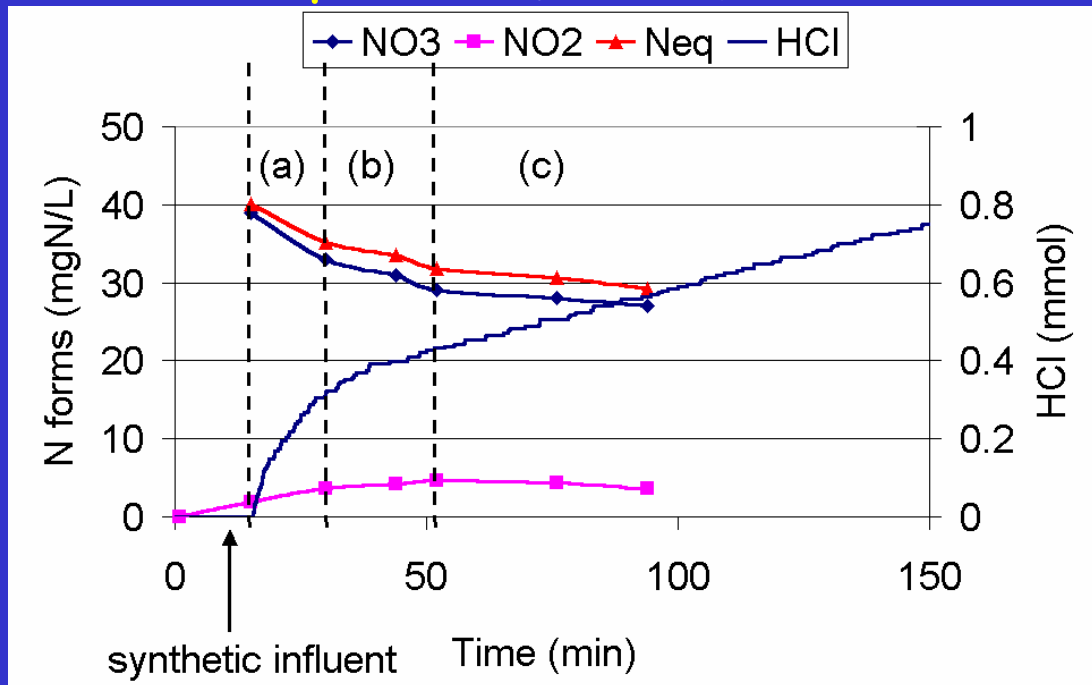
Measured:

- HCl titration curve
- Nitrites+nitrates concentrations

Main objective: Evaluation of the ratio between titration rate and denitrification rate ( $f = \text{mmolH}^+/\text{mgN}$ )

## pH-stat denitrification tests on SBR influent

Test output ( $N_{eq} = NO_3 + 0.6 NO_2$ ).



- (a) denitrification of the rbCOD fraction;
- (b) denitrification of sbCOD;
- (c) endogenous denitrification.

# pH-stat denitrification tests on SBR influent

## Simple model for data interpretation

| Process                                                    | Components                   |                              |     |                   | Rate                                                                                             |
|------------------------------------------------------------|------------------------------|------------------------------|-----|-------------------|--------------------------------------------------------------------------------------------------|
|                                                            | NO <sub>3</sub> <sup>-</sup> | NO <sub>2</sub> <sup>-</sup> | COD | HCl               |                                                                                                  |
| Exogenous denitrification of NO <sub>3</sub> <sup>-</sup>  | -1                           | 1                            | -c1 | f <sub>1es</sub>  | $R_{1es} = R_{1\_MAX} * SSV * \frac{NO_3^-}{NO_3^- + 0.25} * \frac{COD}{COD + 0.1} * 1.1^{T-20}$ |
| Endogenous denitrification of NO <sub>3</sub> <sup>-</sup> | -1                           | 1                            |     | f <sub>1end</sub> | $R_{1end} = R_{1\_end\_MAX} * SSV * \frac{NO_3^-}{NO_3^- + 0.25} * g^{T-20}$                     |
| Exogenous denitrification of NO <sub>2</sub> <sup>-</sup>  |                              | -1                           | -c2 | f <sub>2es</sub>  | $R_{2es} = R_{2\_MAX} * SSV * \frac{NO_2^-}{NO_2^- + 0.8} * \frac{COD}{COD + 0.1} * 1.1^{T-20}$  |
| Endogenous denitrification of NO <sub>2</sub> <sup>-</sup> |                              | -1                           |     | f <sub>2end</sub> | $R_{2end} = R_{2\_end\_MAX} * SSV * \frac{NO_2^-}{NO_2^- + 0.8} * g^{T-20}$                      |

# pH-stat denitrification tests on SBR influent

'f' estimates

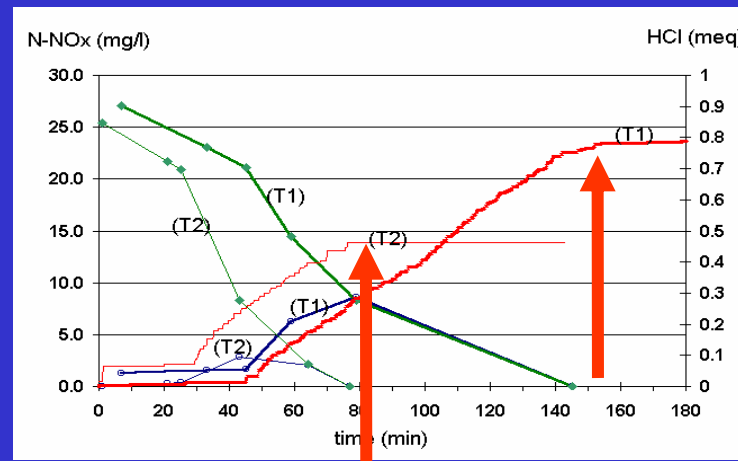
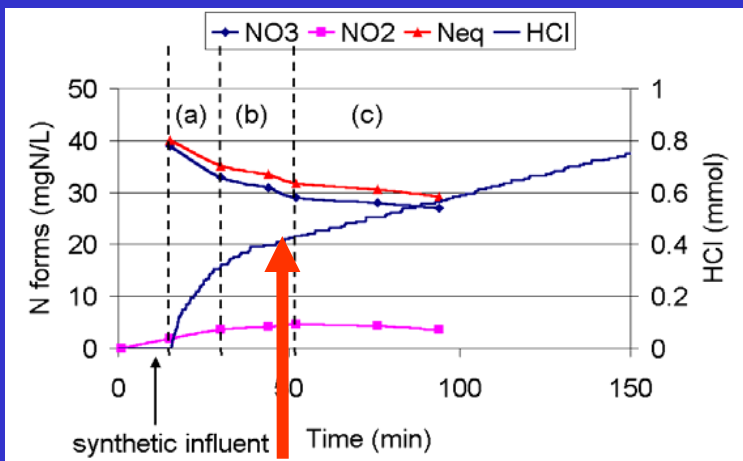
| N form:                      | H <sub>es</sub>                              | H <sub>end</sub> | N form:                      | H <sub>es</sub>                              | H <sub>end</sub> |
|------------------------------|----------------------------------------------|------------------|------------------------------|----------------------------------------------|------------------|
| NO <sub>3</sub> <sup>-</sup> | (meq HCl/mg N-NO <sub>x</sub> <sup>-</sup> ) |                  | NO <sub>2</sub> <sup>-</sup> | (meq HCl/mg N-NO <sub>x</sub> <sup>-</sup> ) |                  |
| mean                         | 0,44                                         | 1,02             | mean                         | 0,73                                         | 1,31             |
| Dev.st. .                    | 0,28                                         | 0,47             | Dev.st. .                    | 0,35                                         | 0,46             |

High variability →

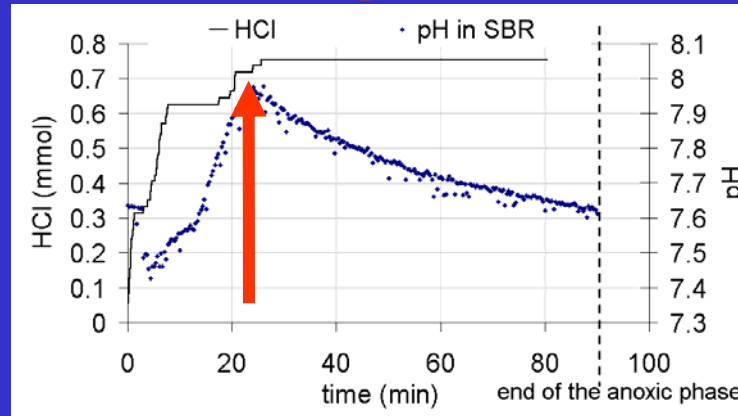
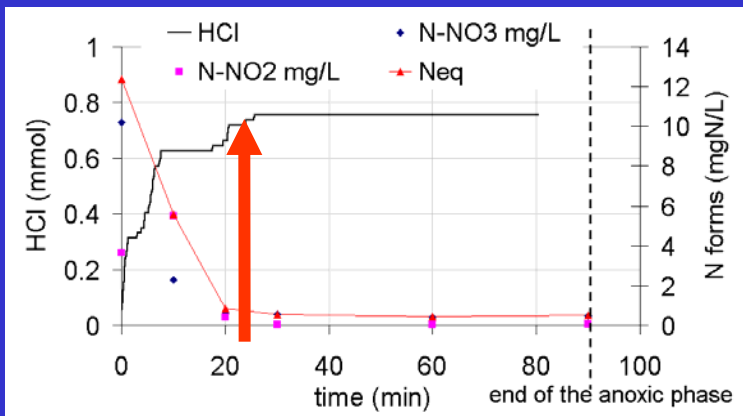
It is less straightforward to assess denitrification activity from titration rate and NO<sub>x</sub> concentration from the amount of acid titrated

# pH-stat denitrification tests on SBR influent

However, qualitative info can be easily obtained:  
(1) End of the denitrification process



Batch tests



Parallel SBR/titration

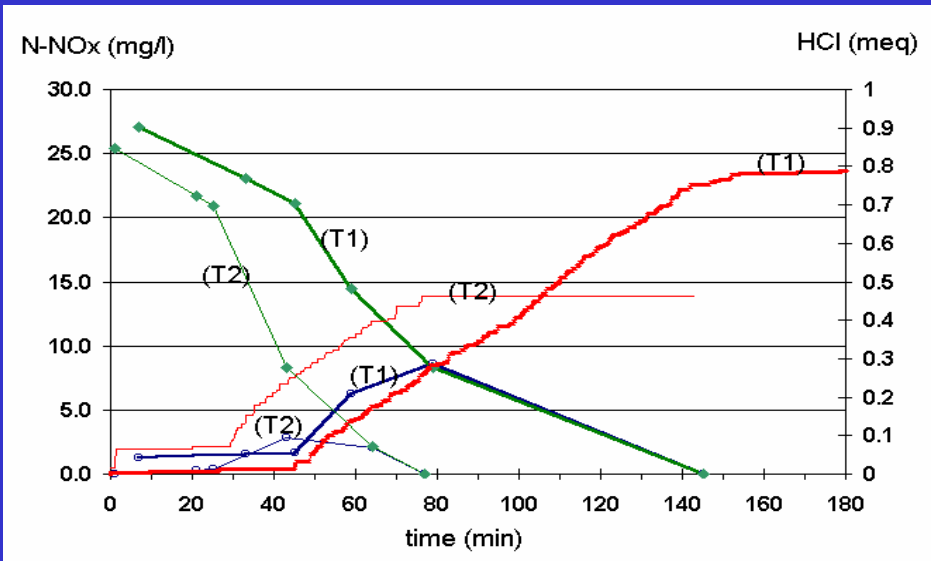
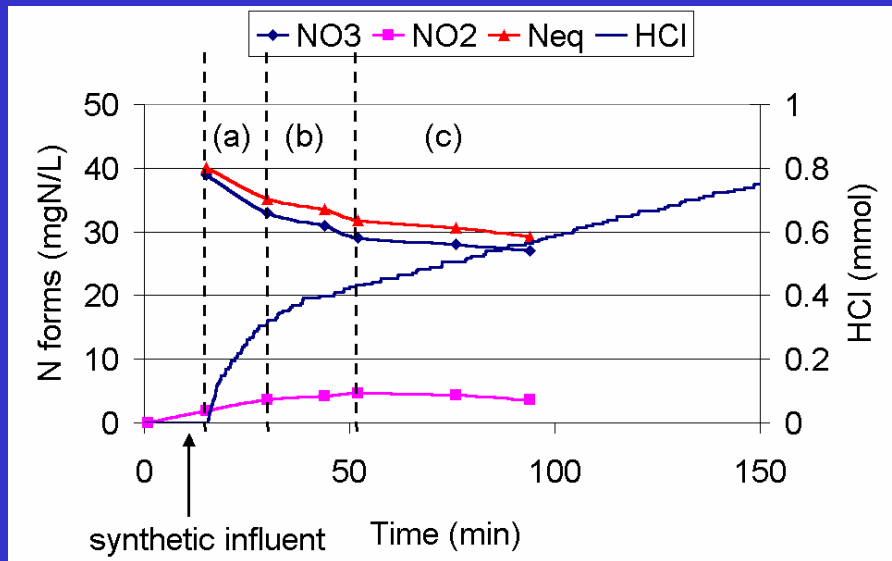
## pH-stat denitrification tests on SBR influent

However, qualitative info can be easily obtained:

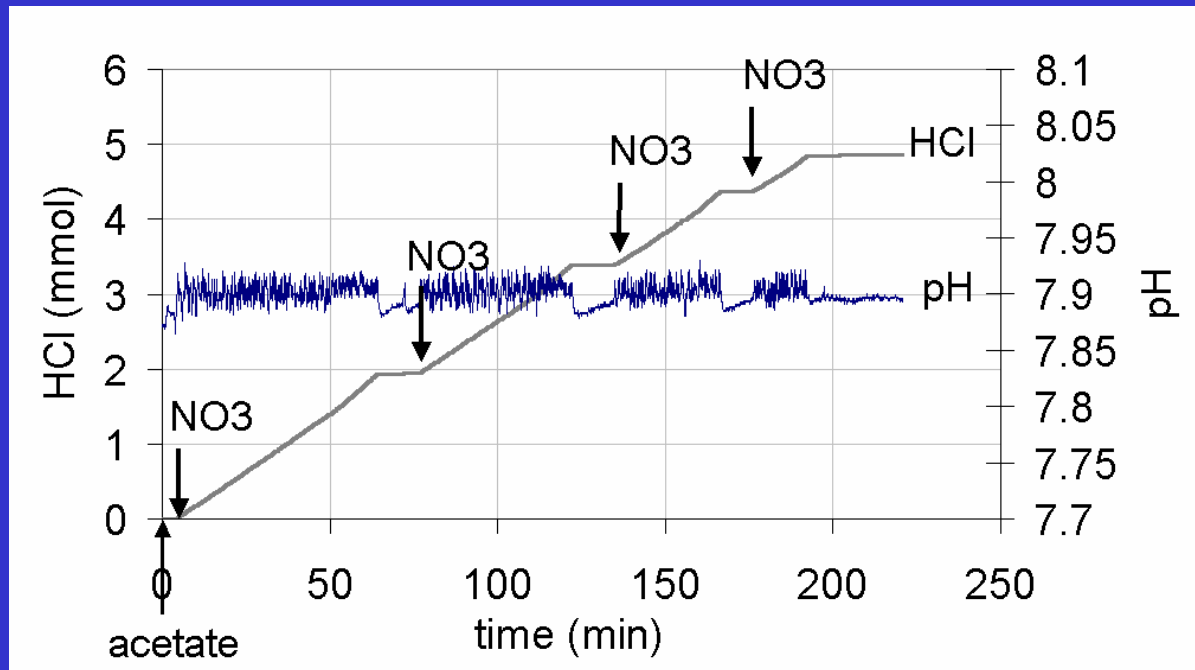
### (2) Limiting substrate

-C limitation:  
residual endogenous  
titration rate

-N limitation: no residual  
titration



## pH-stat denitrification tests on acetate



$$f_{\text{acetate}} = V_{\text{HCl, titrated}} / \text{NO}_{3, \text{dosed}}$$

$$r_{\text{acetate}} = r_{\text{t}} \cdot f_{\text{acetate}} / \text{VSS}$$

## pH-stat denitrification tests on acetate

| $\text{NO}_3^-$ spike<br>(mg N/L) | $f_{\text{acetate}}$<br>(mmol HCl/ mgN- $\text{NO}_3^-$ ) | $r_{\text{den}}$<br>(mgN- $\text{NO}_3^-$ g $^{-1}$ SSV h $^{-1}$ ) |
|-----------------------------------|-----------------------------------------------------------|---------------------------------------------------------------------|
| 5                                 | 0.0967                                                    | 3.41                                                                |
| 10                                | 0.0973                                                    | 3.50                                                                |
| 15                                | 0.0974                                                    | 3.49                                                                |
| 20                                | 0.0948                                                    | 3.49                                                                |

$$f_{\text{acetate}} = V_{\text{HCl,titrated}} / \text{NO}_{3,\text{dosed}}$$

$$r_{\text{acetate}} = r_{\text{t}} \cdot f_{\text{acetate}} / \text{VSS}$$

## pH-stat denitrification tests on acetate

| Test date | $f_{\text{acetate}}$ (mmol HCl/ mgN-NO <sub>3</sub> <sup>-</sup> ) | Test date | $f_{\text{acetate}}$ (mmol HCl/ mgN-NO <sub>3</sub> <sup>-</sup> ) |
|-----------|--------------------------------------------------------------------|-----------|--------------------------------------------------------------------|
| 7-05-04   | 0.098                                                              | 10-05-04  | 0.098                                                              |
| 8-05-04   | 0.100                                                              | 10-05-04  | 0.107                                                              |
| 8-05-04   | 0.114                                                              | 10-05-04  | 0.104                                                              |
| 8-05-04   | 0.116                                                              | 10-05-04  | 0.100                                                              |
| 8-05-04   | 0.116                                                              | 10-05-04  | 0.098                                                              |
| 8-05-04   | 0.114                                                              | 10-05-04  | 0.092                                                              |
| 9-05-04   | 0.096                                                              | 10-05-04  | 0.101                                                              |
| 9-05-04   | 0.096                                                              | 14-06-04  | 0.166                                                              |
| 9-05-04   | 0.083                                                              | 15-06-04  | 0.169                                                              |
| 9-05-04   | 0.107                                                              | 18-06-04  | 0.142                                                              |
| 10-05-04  | 0.100                                                              | 24-06-04  | 0.101                                                              |

A relevant variability is still observed

## pH-stat denitrification tests on acetate

Procedure to assess nitrate concentration:

- *step 1*: a non-limiting concentration of acetate is dosed to the nitrate-containing sludge sample; pH-stat titration is performed until a plateau is observed, i.e. until nitrates are fully denitrified and the amount of acid dosed is recorded ( $V_{\text{HCl,sludge}}$ );

- *step 2*: a known amount of nitrates ( $\text{NO}_{3,\text{spike}}$ ) is added to the same sludge sample; pH-stat titration is continued until a second plateau is reached and the amount of acid dosed after the nitrates spike is recorded ( $V_{\text{HCl,spike}}$ ).

$$f_{\text{acetate}} = V_{\text{HCl,spike}} / \text{NO}_{3,\text{spike}}$$

$$\text{NO}_{3,\text{sludge}} = \text{NO}_{3,\text{spike}} \cdot V_{\text{HCl,sludge}} / V_{\text{HCl,spike}} = V_{\text{HCl,sludge}} / f_{\text{acetate}}$$

## pH-stat denitrification tests on acetate

Results:

| Test date | mg NO <sub>3</sub> <sup>-</sup> /L<br>estimated by pH-stat titration | mg NO <sub>3</sub> <sup>-</sup> /L<br>analytical determination |
|-----------|----------------------------------------------------------------------|----------------------------------------------------------------|
| 14-06-04  | 9.0                                                                  | 10                                                             |
| 15-06-04  | 10.8                                                                 | 10                                                             |
| 18-06-04  | 13.3                                                                 | 13                                                             |

More tests are in progress