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MELISSA

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TECHNICAL NOTE : 77.1

Validation of the nitrite estimator from experimental data

(ESTIMATOR BASED ON THE NITROGEN BALANCE)

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0	0	June 2004	Draft
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Abbreviations or notations:
NH_3 : ammonia (gaseous or solvated) or ammonium ion
NO_2 : nitrite ion
NO_3 : nitrate ion
SO4 : sulphate ion
PO4 : phosphate ion
N_s : Nitrosomonas strain
N_b : Nitrobacter strain

1. INTRODUCTION

The estimator, extracted from the LGCB First Principles model of the column and based on the Nitrogen element conservation, has been elaborated in TN 73.2. It is now evaluated from experimental data acquired on the pilot plant at UAB.

2. THRESHOLD OF NO2 DETECTION

The estimation of NO_2 concentration at column output, b_3, has been established in relation (7bis) of TN73.2 as follows:

$$b_3 = \beta_1 \cdot b_1 + \beta_2 \cdot b_2 - \frac{1}{H} \cdot \left(\beta_1 \cdot d_{i1} + \beta_2 \cdot d_{i2}\right) \quad (1)$$

where :

b_1 and b_2 are the NH_3 and NO_3 concentrations in the liquid phase at column output;

d_{i1} and d_{i2} are the NH_3 and NO_3 concentrations in the liquid phase at column input;

1/H is a dynamical transfer whose static gain is 1;

β_1 and β_2 are coefficients given by the First Principles model, function of stoechiometry and half saturation constants.

Considering:

- the estimation at steady state ($\Rightarrow$ 1/H = 1);
- $\beta_1 \approx -1$ and $\beta_2 \approx -1$ (relations (A3.5) and (A3.8) in TN 73.2);
- $d_{i2} = 0$ (no nitrate at column input or negligible);
- $b_1 << b_2$ (NH3 is nearly completely transformed into NO3 at column output);

then

$$b_3 \approx d_{i1} - b_2 \quad (\text{at steady sate}) \quad (2)$$

and the standard deviation on NO_2 estimation, σ_3, can be expressed from standard deviation on measurements of NH_3 at column input, σ_1, and NO_3 at column output, σ_2, as follows :

$$\sigma_3 = \alpha \cdot \left(\sigma_1 + \sigma_2\right) \quad (3)$$

where:

α depends on the coefficient of the low pass filter (α = 0.3 , for the present estimator; justification in annex 2).

One can assume that, in a general way, a variable x is detected if its relative range of error is lower than 50 % (or in other words, an absolute range [5 15] ppmN could be acceptable for an actual NO2 value of 10 ppmN):

$$\frac{\delta x}{x} \leq 0.5 \quad (4)$$

Now, assuming a normal (Gauss) distribution of the points, they are within 3 times the standard deviation around their mean value, with a probability of 95%.

So $\delta x = 3 \cdot \sigma$ (5)

Then $b_3 \geq 6 \cdot \alpha \cdot \left(\sigma_1 + \sigma_2\right)$ (6)

which can be related to the load di1 :

$$\frac{b_3}{d_{i1}} = 6 \cdot \alpha \cdot \left(\frac{\sigma_1}{d_{i1}} + \frac{\sigma_2}{d_{i1}} \right) \approx 6 \cdot \alpha \cdot \left(\frac{\sigma_1}{d_{i1}} + \frac{\sigma_2}{b_2} \right) \quad (7)$$

In the present case, the error on the NH3 measurement at column output can be assumed zero because the concentration is very well known. So, in that case only, the condition (7) above can be simplified and the threshold of NO2 detection related to the load d_{i1} can be expressed as:

$$\frac{b_3}{d_{i1}} \approx 6 \cdot \alpha \cdot \frac{\sigma_2}{b_2} \quad (8)$$

According to the Technical Note 52.22 (draft) by UAB p.18, the relative standard deviation, $\frac{\sigma_2}{b_2}$, is 6-9 %.

Then, in the present case where the error of measurement on the input load of ammonia is zero, the minimum value of NO_2 that can be estimated is:

$$b_{3\min} = 6 \cdot 0.3 \cdot 0.09 = 16\,\% \text{ of the ammonia load } d_{i1} \quad (9)$$

Illustration :

To illustrate the relation (8) above (where α=0.3 in the case of the present estimator) :

$$\frac{b_{3\min}}{d_{i1}} \approx 2 \cdot \frac{\sigma_2}{b_2} \quad (10)$$

two simulations are done where the NO_2 at steady state is twice or half the threshold b_{3min}.

The 2 simulations represent a step of flow rate (from 0.4 to 0.6 l/h) where :

- the NO_3 concentration at column output, b_2, is about 0.023 mol/l ;
- the NH_3_total concentration at column input, d_{i1}, is about 0.025 mol/l ;
- the NO_2 concentration at steady state is about 2.10^{-4} mol/l .

The standard deviations simulated are 1.25 and 5 10^{-4} mol/l .

simulation	standard deviation on NO_3 σ_2 (mol/l)	threshold b_{3min} (mol/l)	NO_2/threshold
1 (figure 1)	1.25 10^{-4}	1 10^{-4}	2
2 (figure 2)	5 10^{-4}	4 10^{-4}	0.5

When NO_2 is twice the threshold, it can be detected (bottom graph of figure 1) and when it is half the threshold it cannot (bottom graph of figure 2).

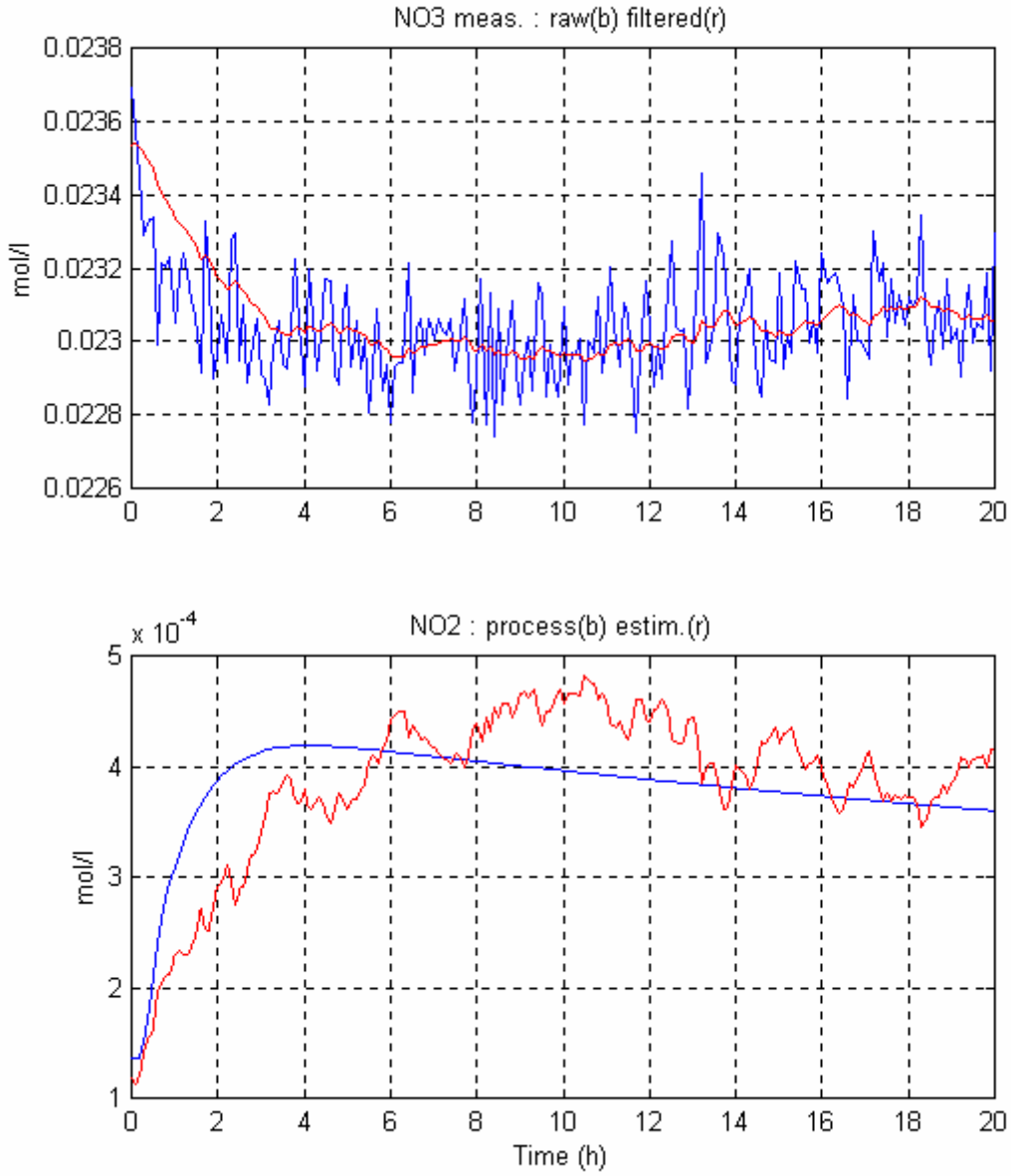

Figure 1 : NO_2 = twice the threshold

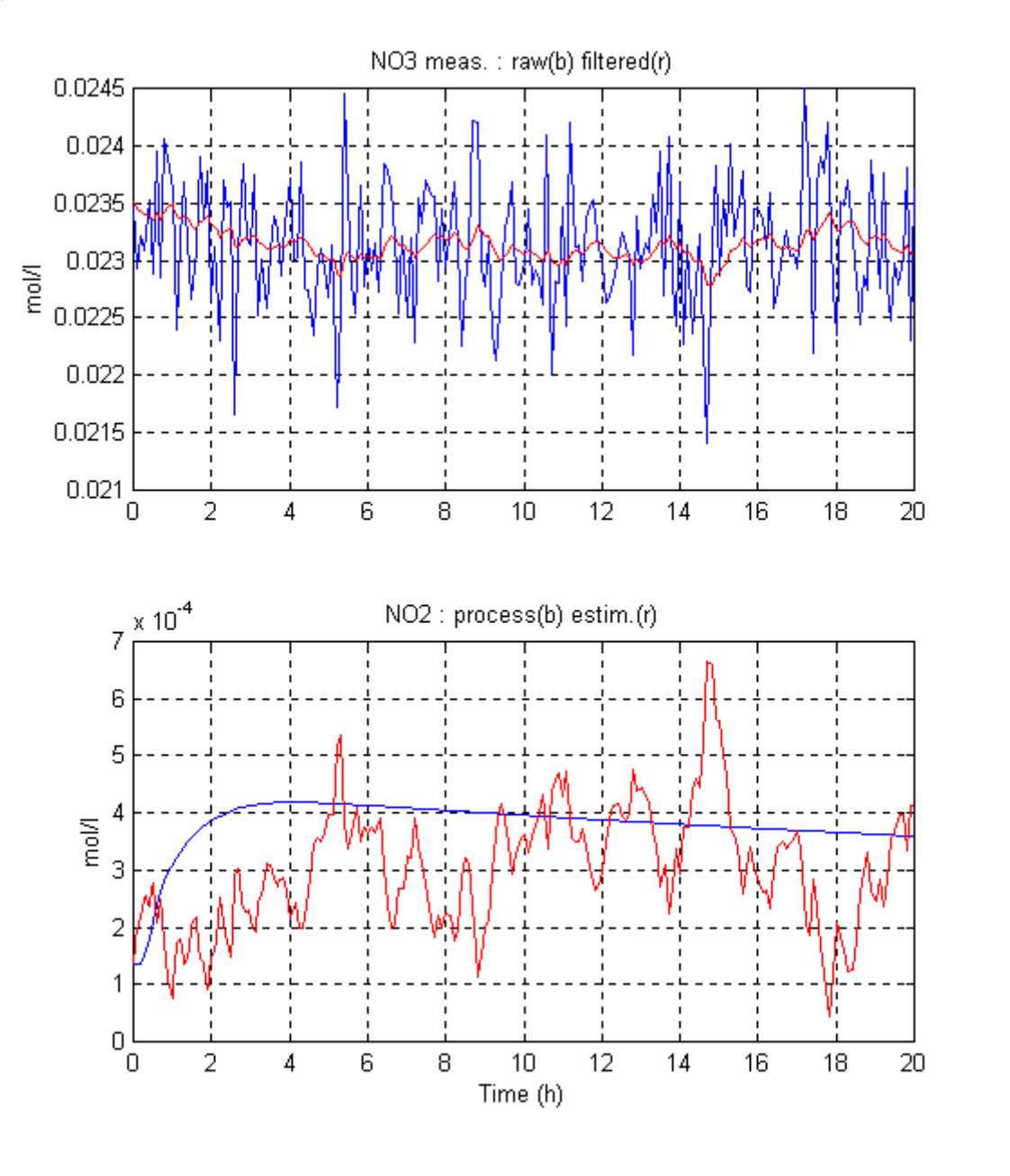

Figure 2 : NO_2 = half the threshold

3. UAB TESTS

3.1. Tests from April 29th to May 16th 2003

UAB has realized the tests requested in TN 48.3 (ADERSA) p.19 . They are reported in the note 'Progress Meeting – 01/04/03'. Unfortunately, at the moment when the TN 48.9 has been written, the range of error on the NH_3 and NO_3 measurements was not evaluated yet. And the

UAB tests show very low concentrations of NO_2, far lower than the threshold of detection of the relation (9).

Step of ammonia from 300 to 600 ppmN :

Among these tests, one produces a peak of NO_2 of 15 ppmN, which represents the highest value in all the UAB tests : it is the one related to a step of ammonia concentration (from 300 to 600 ppmN) from May 14^{th} to 16^{th} 2003, plotted in the figure 3. Although it is under the level of detection, the estimator was fed with it. The resulting estimation of NO_2 is shown on the top graph of the figure 3 : due to the high noise of the NO_3 measurements, the estimation of NO_2 is highly noisy too and does not fit the measurements of NO_2.

Moreover a measured NO2 peak occurs at time t=33h when there is no process excitation (step of ammonia); in fact the process excitation has been done at t=3h. Probably this NO2 peak is not correlated to the ammonia step and is the result of disturbance in the column. The estimator is not able to detect it. Contrarily it 'detects' NO2 peaks (between t=5 and t=31 h) when the measurements of NO2 are nearly null.

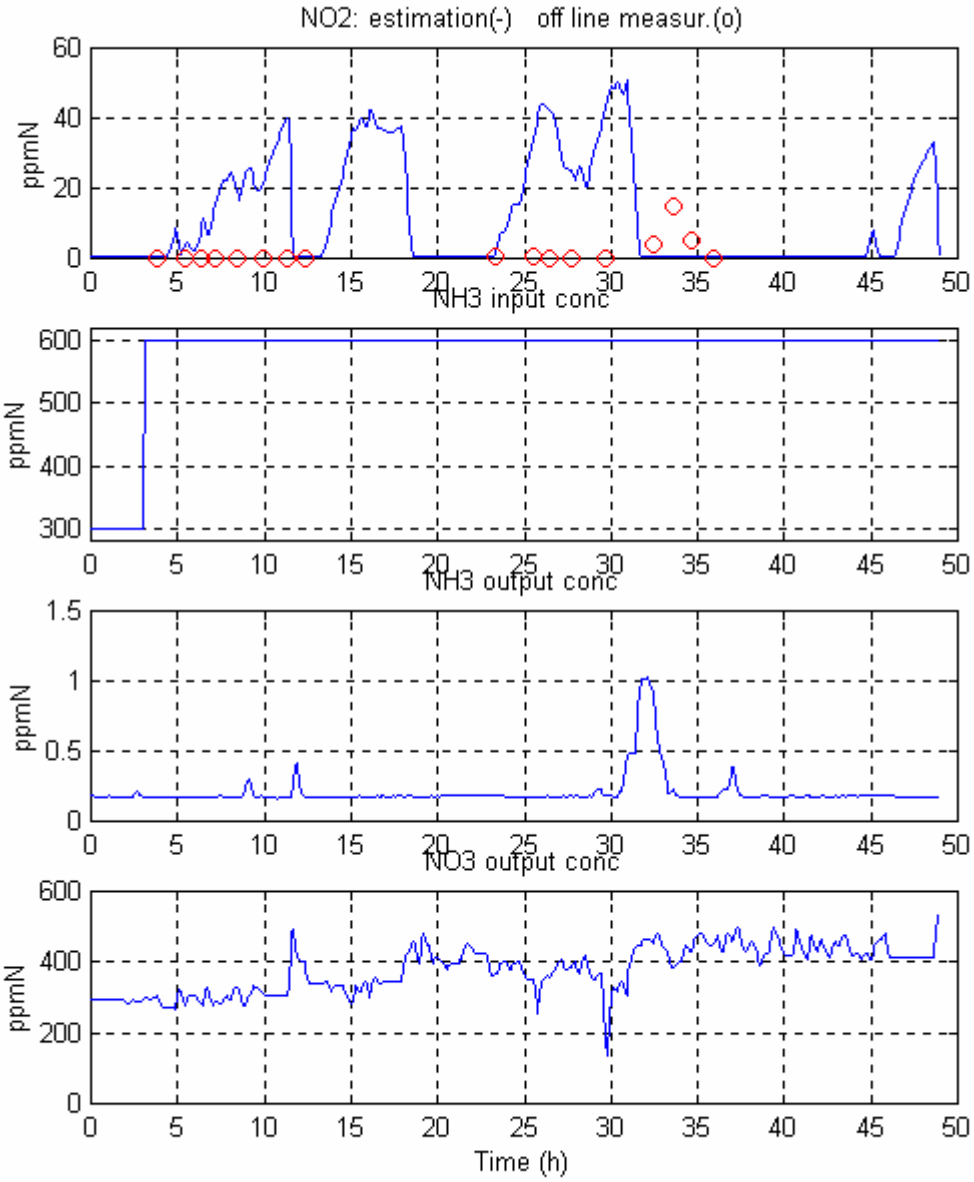

Figure 3 : Estimation of NO2 from UAB test (ammonia step; May 14th to 16th 2003)
Estimation of NO2 : continuous blue line of the top graph
Measurements of NO2 : red 'o'

Remark : The raw data coming from UAB files have been put into the required format for the estimator (details in annex 1).

3.2. Test of variation of Dissolved Oxygen from May 23rd to June 30th 2000

This test has been studied already in TN 48.3 (by ADERSA) p.13 with the estimator at that moment. Since some modifications have been done on it, the estimator is checked again. The estimation of NO2 (figure 4) is identical to the one of the TN 48.3 .

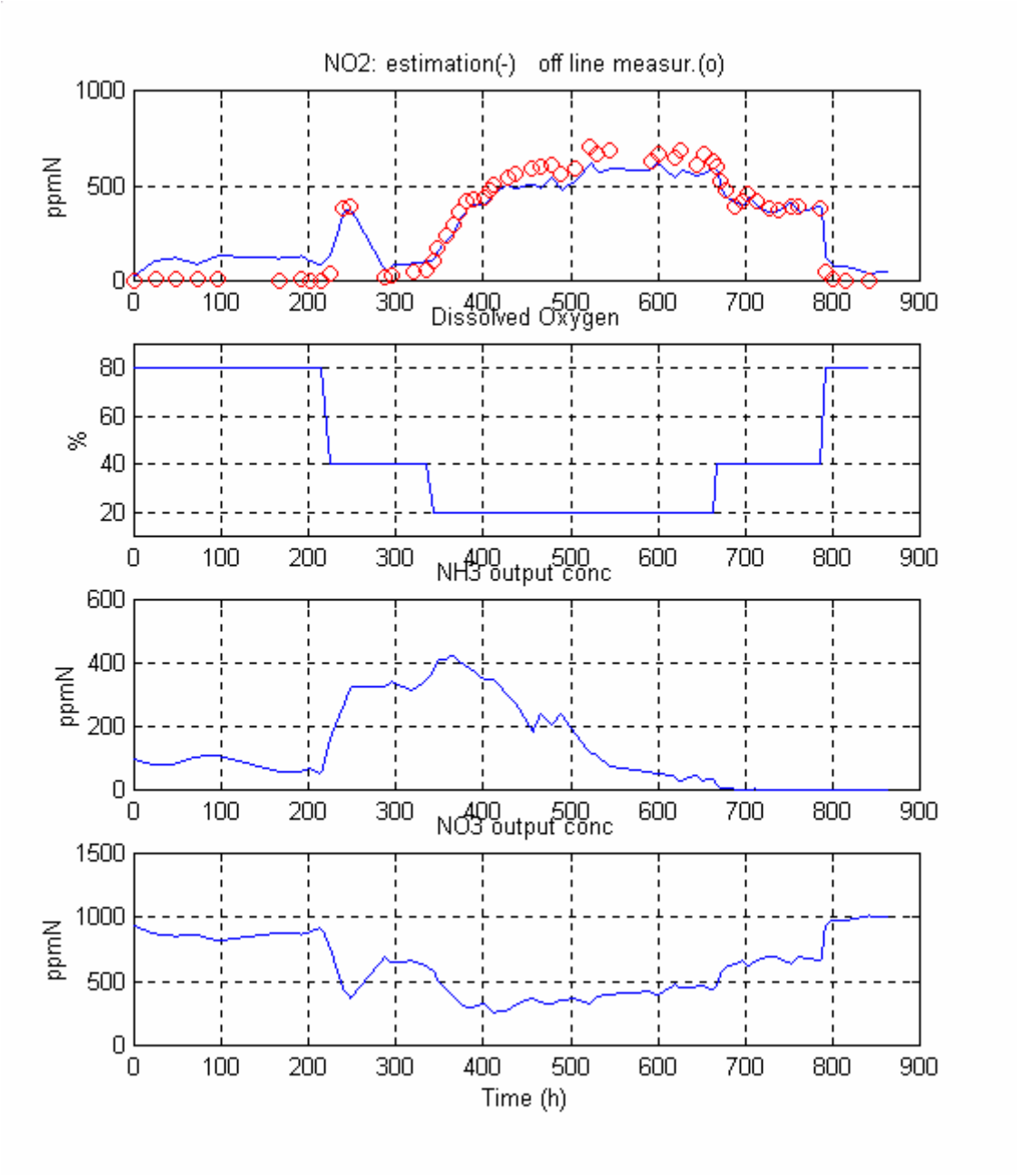

Figure 4 : Estimation of NO2 from UAB experiment (DO; May 23rd to June 30th 2000)
Estimation of NO2 : continuous blue line of the top graph
Measurements of NO2 : red 'o'

4. CONCLUSION

The present estimator, extracted from the LGCB First Principles model of the column and based on the Nitrogen element conservation, has been tested on the UAB pilot plant. As foreseen from the level detection rule (section 2), it gives quite good estimation of NO2 when its concentration is high (more than 100 ppmN of the test in section 3.2) but it is unable to estimate the current low concentration (less than 0.1 ppmN) of a normal operating process (test of section 3.1).

It is foreseen to build a Kalman filter based on the whole model of the column in order to improve the estimation of low NO2 concentration.

5. ANNEX 1 : RECONSTRUCTION OF DATA FROM UAB TESTS

5.1. Preparation of data for the estimator

Among the whole experiment (from April 29th to May 16th 2003), a part corresponding to the step of ammonia concentration has been selected from May 14th 10:12 till the end.
A lack of data has been rebuilt from May 14th 10:12 during 2.5 h : the lacking ammonia concentration has been set to the probable value of 295 ppmN (script 'prepdata.m' of the directory 'step300_600ppmN').
According to UAB (email on June 17th 2003), data are acquired every minute, measurements of NH3 and NO3 at column output are done every 16 minutes and the delay due to the sensors and analysers is 1.1 h. So :

- Data on NH3 and NO3 have been shifted to cancel the delay;
- Data have been filtered and sampled at period of time of 0.1 h (sampling period of the estimator).

Then data have been saved in a file to the required format for the estimator.

5.2. Software of preparation of data for the estimator

```
% Preparation of the raw data from UAB for the NO2 estimator
% (data from ASCII files in the directory 'UABdata2\step300_600ppmN'
% ------------------------------------------------------------------
% The data resulting from this script will feed a C programme
% calling the main function of the estimator 'nctrl.c'

clear
titre = 'UAB data from May 14th 10:02  to 16th 12:13 2003';
% 1_ First step : pre-preparing a pre-data mat.file 'essaiprt.mat'
if 0
  nomf = ['NT030514';'NT030515';'NT030516'];
  [m,n]=size(nomf);

  for i = 1:m
    nomfic = nomf(i,:);
    eval(['load ',nomfic,'.txt'])
    if i == 1
      eval(['[m n] = size(',nomfic,')'])
      eval(['res = ', nomfic,'(:,3:n);'])
      eval(['temps = ', nomfic,'(:,1:2)*[1; 1/60];']) % time (h)
    else
      eval(['[m n] = size(',nomfic,')'])
      eval(['res = [res;', nomfic,'(:,3:n)];'])
      eval(['t = ', nomfic,'(:,1:2);'])
      t(:,1)=t(:,1)+24*(i-1); % incrementing the number of days
      temps = [temps; t*[1; 1/60]];   % time (h)
    end
```

```
    eval(['clear ',nomfic,';']);
  end
  temps=temps-temps(1);
  save essaiprt temps res % saving part of the test
else
  load essaiprt
end
% Sequence of data in the files 'NT*.txt' (conc in ppmN)
%Hours Minute NitrDo.value NitrDo.sp NitrDoTop.value NitrDoTop.Bot
%NitrpH.value NitrpH.sp NitrpHTop.value NitrpHBot.value
%NitrTemp.value NitrTemp.sp NitrTempTop.value NitrTempBot.value
%NitrPressure.value NitrPressureSP.value NitrAmCon.value NitrNitrCon.value
%NitrAmCon.sp NitrNitrCon.sp
libel =['DoMeas      ';'DoSp        ';'DoTopMeas   ';'DoTopBot    '; ...
        'pHMeas      ';'pHSp        ';'pHTopMeas   ';'pHBot       '; ...
        'TempMeas    ';'TempSp      ';'TempTopMeas ';'TempBot     '; ...
        'PressureMeas';'PressureSp  '; ...
         'AmmoniaMeas ';'AmmoniaSp   ';'NitrateMeas ';'NitrateSp   '];

% 2_ Second step : Preparing the file of data for the controller
% Rebuilding the corrupted data of NO3 during the 2.5 first hours
ind=find(temps<=2.5);
res(ind,17)=295*ones(size(ind)); % (ppmN) assumed value of NO3 (instead of the corrupted value
: 40)

% Taking into account the dead time of the NO3 and NH3 sensors
tdelay=1.1; % (h) dead time at flow=0.15 l/h according to Julio Perez email on June 17th 2003
ind=find(temps<=tdelay);
m=length(ind);
cNH3o=res(m+1:size(res,1),15); % shifted NH3 at column output
cNO3o=res(m+1:size(res,1),17); % shifted NO3 at column output
temps=temps(1:length(temps)-m);% shortening time vector for plotting

% Filtering before sampling
% 1. Rebuiding the lacking data at the sampling period of 1 mn
dt_r=1/60; % (h)
T_r=0:dt_r:temps(length(temps));
y=interp1(temps,[cNH3o,cNO3o],T_r);
% 2. Filtering
alpha=exp(-1/6); % 1 sample among 6
alpha1=1-alpha;
z(1,:)=y(1,:);
for i=2:length(T_r)
  z(i,:)=alpha*z(i-1,:)+alpha1*y(i,:);
end
% 3. Over-sampling
dt_e=.1; % (h) sampling period of the estimator
T_e=[0:dt_e:temps(length(temps))]';
cNH3os=interp1(T_r,z(:,1),T_e); % over-sampled NH3
cNO3os=interp1(T_r,z(:,2),T_e); % over-sampled NO3

% Step of concentration of ammonia in the input flow
cNH3i=300*ones(size(T_e)); % initial input conc : 300 ppmN
t0=3.1; % (h) step of ammonia on May 14th 13:10; starting of the data : May 14th 10:02
ind = find(T_e>=t0);
cNH3i(ind)=600*ones(size(ind)); % step at t0
% Plotting the data necessary to estimation of NO2 and biomass
fen2tr
subplot(411)
   plot(T_e,cNH3i), grid
   title('NH3 input conc')
   ylabel('ppmN')
subplot(412)
   plot(temps,cNH3o,T_e,cNH3os), grid
   title('NH3 output conc')
   ylabel('ppmN')
subplot(413)
   plot(temps,cNO3o,T_e,cNO3os), grid
   title('NO3 output conc')
   ylabel('ppmN')
xlabel('Time (h)');
trtitre(gcf,titre,date)
```

```
% Writing the data file for estimator
% Input 'u'
%       u(1)                          (l/h)   liquid flow rate
%       u(1+[1:NG])                   (mol/l) conc. in the Gas input flow
%       u(1+NG+[1:NG+NL])             (mol/l) conc.(total form for the biphasis compounds) in
the Liquid input flow
%       u(1+2NG+NL+[1:NG,NG+[2:NL]])(mol/l) conc. of O2 CO2 NH3 NO3 PO4 SO4 in the L output
flow
%                                             (total form for the biphasis compounds)
%       u(3NG+2NL+1)                  (l/h)   gas flow rate
%       u(3NG+2NL+2)                  (l/h)   required liquid flow rate
%       u(3NG+2NL+3)                  (mol/l) NO2 setpoint (or NO2 max constrain)
%       u(3NG+2NL+4)                  (mol/l) compensation term on NO2 estimation
dimi_c=21; % size of the inputs vector
m=length(T_e);
u=zeros(m,dimi_c);
u(:,1) =.15*ones(m,1); % (l/h) liquid flow rate of the test
u(:,2) =7e-3*ones(m,1);% (mol/l) conc of O2 in the Gas input flow
                       % arbitrary value to avoid error detection
u(:,7) =cNH3i*1e-3/14; % (mol/l) conc. of total NH3 in the Liquid input flow
u(:,14)=cNH3os*1e-3/14;% (mol/l) conc. of total NH3 in the Liquid output flow
u(:,15)=cNO3os*1e-3/14;% (mol/l) conc. of NO3 in the Liquid output flow
u(:,19)=.15*ones(m,1);% (l/h) required liquid flow rate
if 0 % Saving in directory 'validV3C' for test with Version 1 of the estimator/controller
   save ..\..\..\validV3C\f_data.txt m u -ASCII
  save ..\..\..\validV3C\f_data  m u
else% Saving in directory 'validV4C' for test with evolutionary Version of the
estimator/controller
   save ..\..\..\validV4C\f_data.txt m u -ASCII
   save ..\..\..\validV4C\f_data  m u
end

% Plotting the whole set of original data of files 'NT*.txt'
if 0
imax=[4 4 4 2 4];
k=0;
for i=1:5
  fen2tr
  for j=1:imax(i)
    k=k+1;
     subplot(4,1,j);
     plot(temps,res(:,k)); grid
     title(libel(k,:))
     %ylabel('')
    %v=axis;
  end
   xlabel('Time (h)');
   trtitre(gcf,titre,date)
end
end
```

5.3. Software in C language for running the estimator

/* Main for running the estimator/controller with data from a file where the data are read line after line */

```
#include <math.h>
#include <stdio.h>
#include "c:\melissa\cvsML5_3\nitri\regulV4C\comc\global.h"

void main()
{
  /* Internal variables */
   int j, k;
   double valfic;
   /* REALN u[kmax][DIMIC];
   REALN cNO2e[kmax], cNse[kmax], cNbe[kmax]; */
   REALN flag_sav,   flag_ini;
   REALN timecount, dt_e={0.1};
  REALN R_x[DIMXE+DIMXC+DIMIC],R_u[DIMIC];
```

```
  REALN errors[5];
  FILE *pf1, *pf2;

  /* Opening results file */
  pf2 = fopen("f_est.txt", "w");
  /* Opening data file */
  if ((pf1 = fopen( "f_data.txt", "r")) == NULL)
  {
     printf("Data file f_data.txt does not exist\n");
     exit(0);
  }
  printf("Reading data file and estimating \n");

  fscanf(pf1, "%lf", &valfic);
  k = (int)valfic;
  printf("Number of samples : \t%5.0d\n",k);
  timecount = -dt_e;  /* Init time counter */
  flag_ini=0.;        /* Init flag of estimation */
  flag_sav=1.;        /* for saving intermediate variables of 'nctrl' */
  j=0;
  while (fscanf(pf1, "%lf", &valfic) != EOF)
  {
     R_u[j]=(REALN)valfic;  j++;
     if (j==DIMIC)
     {
        j=0;
       /* Calling the main control subroutine 'NCTRL' for estimation of NO2 and biomass*/
        nctrl(R_x, errors, R_u, flag_sav, &flag_ini);
        timecount += dt_e; /* Incrementing time */
        /* Displaying error code to screen */
        if (errors[0] > 0)
           printf("Time (hour); Error num; Error code:  %15.4e%6d%6d%6d\n",
                     timecount,(short)errors[0],(short)errors[1],(short)errors[2]);
        if (pf2 != NULL) /* saving estimation of Ns, Nb Biomasses and NO2 on ASCII file */
       fprintf(pf2, "%13.4e%13.4e%13.4e\n", R_x[21],R_x[22],R_x[25]);
     }
  }
  fclose(pf1);
  fclose(pf2);
}
```

6. ANNEX 2: Low Pass filter

The standard deviation of a random signal is reduced when it is filtered through a low pass filter (figure A2.1).

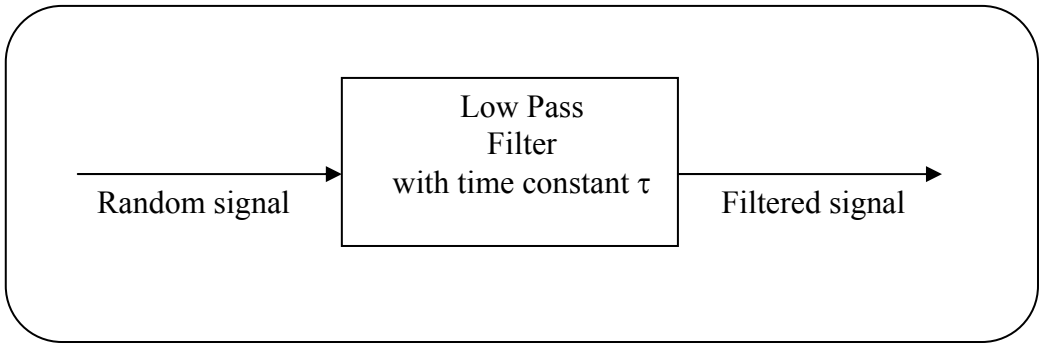

Figure A2.1 : Low Pass Filter

The reduction coefficient can be evaluated in simulation (figure A2.1).
The simulation shows that the standard deviation of the random signal (equal to 1) is reduced to 0.3 at the filter output. The reduction coefficient 0.3 is the parameter 'α' of the formula (3).

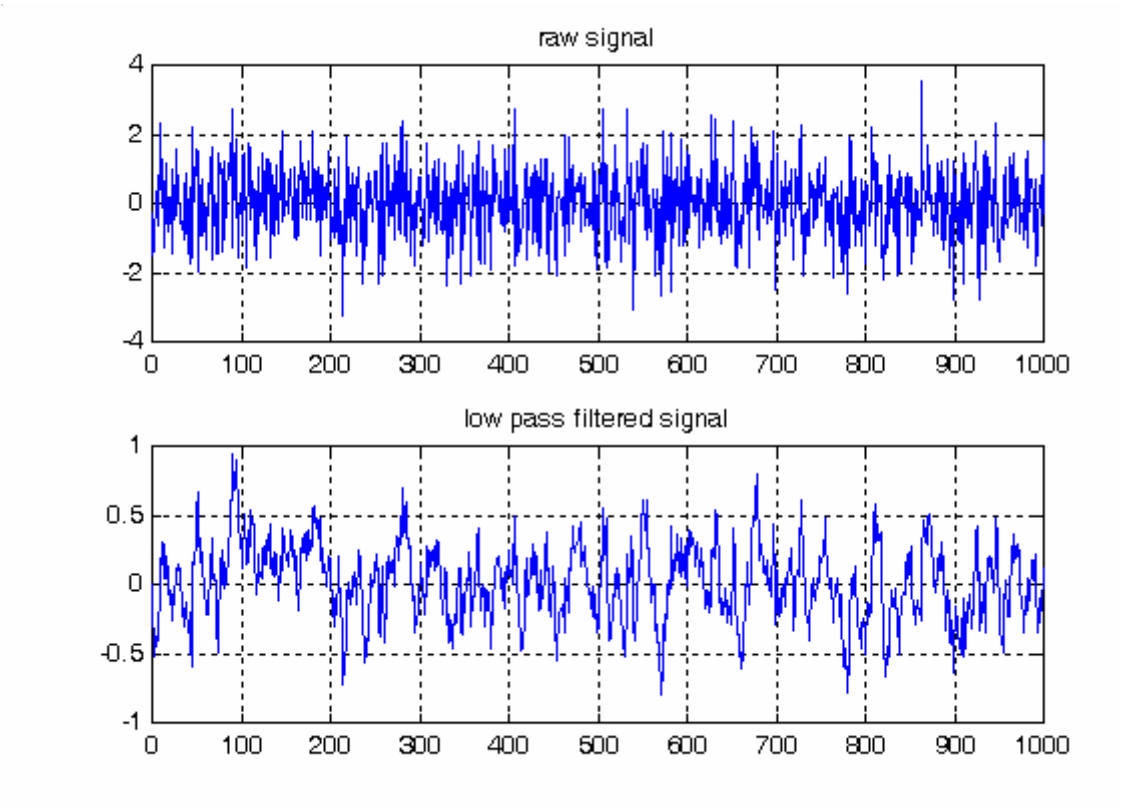

Figure A2.1: Random signal filtered through a Low Pass filter
Upper graph: random signal (mean value: 0; standard deviation: 1).
Lower graph: filtered signal (mean value: 0; standard deviation: .3).

When the time constant τ increases, the coefficient α decreases and the detection threshold is more narrow (in other words better). The consequence is that the de-phasing increases too and a variation of NO2 can be estimated too late. So a trade-off is done.