



# THE POTENTIAL OF OFF-GAS ANALYSES FOR MONITORING WASTEWATER TREATMENT PLANTS

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## ABSTRACT

Continuous CO<sub>2</sub> and O<sub>2</sub> measurements in the exhaust gas of wastewater treatment plants have been simulated to study their significance for fast process monitoring. More specifically, the question was raised whether the ratio of the carbon dioxide production rate to the oxygen consumption rate (the RQ value) can be used to distinguish C-oxidation from N-removal (nitrification or combined nitrification-denitrification). Although the oxygen uptake rate and carbon dioxide production rate by the micro-organisms are indicative indeed, these rates can not very well be monitored in the gas phase mainly due to the additional CO<sub>2</sub> production accompanying alkalinity consumption. Only large changes in nitrification activity can be monitored this way. The RQ is however a strong measure for the COD/TOC ratio of the converted waste. Combination of RQ measurements with TOC measurements can therefore probably replace laborious COD measurements. In plants with combined C-removal and nitrification, the difference in in- and effluent alkalinity is a measure for nitrification. If NH<sub>3</sub>-removal is determined, the biomass production rate can be calculated from the gas flow rate in combination with the exhaust CO<sub>2</sub> and O<sub>2</sub> measurements. Copyright © 1996 IAWQ. Published by Elsevier Science Ltd.

## KEYWORDS

C-removal; biomass production rate; carbon dioxide production rate; denitrification; gas analysis; nitrification; oxygen uptake rate; monitoring; respiratory coefficient; wastewater.

## INTRODUCTION

Paramagnetic and infra-red techniques for measuring respectively gas phase O<sub>2</sub> and CO<sub>2</sub> concentrations are robust, accurate, relatively cheap and are widely used in fermentation plants. Off-gas analysis for on-line monitoring and control of wastewater treatment plants has until now gained rather limited attention. Oxygen measurements in off-gas have been reported for monitoring the oxygen transfer rate (Daigger *et al.*, 1992), or in relation to dissolved oxygen control (Tanuma *et al.*, 1981). The use of the oxygen uptake rate as an important measure for plant performance has been very well recognised (Watts and Garber, 1993), but measurements are almost invariably carried out in the liquid phase with in situ dissolved oxygen probes (Holmberg *et al.*, 1989; Sollfrank and Gujer, 1990) or eventually with respirometers (Spanjers *et al.*, 1994). Measurements of gaseous carbon dioxide concentrations are to the knowledge of the authors not practised in plants at all. Practical problems including collection of the gas sample, and unfavourable ambient conditions

for proper instrument functioning have been reported to be the reason for this situation. For carbon dioxide measurements another reason may be the more fundamental problem, that produced CO<sub>2</sub> is only partly transferred to the gas phase.

Off-gas analysis has many advantages over measurements in the liquid phase. Gas samples are taken from a large, well mixed gas flow leaving the reactor so that the concentration levels reflect an overall reactor performance, whereas a probe in the liquid phase is rather a "point measurement". Pre-treatment of gas samples is simple. Costs for equipment maintenance are relatively small and no chemical reagents are required. Investment costs are comparable to those for wet chemical liquid phase analyses (e.g. nitrate or phosphorus). It may be clear that with more and more treatment plants are becoming covered (or even built underground) in densely populated areas, off-gas analyses are worthwhile to be considered as an alternative or an addition to liquid phase analysis.

The central question in this paper is to analyse theoretically whether carbon dioxide and oxygen measurements in the gas phase can give a direct evaluation of C-removal, nitrification and/or denitrification. Influences of sludge age, the decay coefficient, the COD/TOC ratio of the converted substrate and alkalinity on these measurements will be considered.

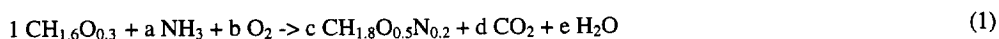
## INTRINSIC CONVERSION RATES FOR OXYGEN AND CARBON DIOXIDE

### Introduction

The exhaust gas phase composition in terms of oxygen and carbon dioxide results from biomass activity and from the distribution of oxygen and carbon dioxide over the liquid and gas phases. For the latter, especially the pH-dependent carbon dioxide-bicarbonate equilibrium is important. In this section, we will examine the intrinsic oxygen uptake rate (OUR) and carbon dioxide production rate (CPR) that result only from biomass activity. These intrinsic rates are not directly measurable, but show the limits of what can be observed from the OUR and CPR. The conversion rates are derived explicitly for C-removal, nitrification and denitrification. In the subsequent section, a simple steady-state reactor model will be used to calculate the gas phase concentrations for simultaneous C and N removal, taking the gas-liquid distribution of oxygen and carbon dioxide into account.

### C-removal

The following macro-chemical equation lists the compounds that significantly contribute to the heterotrophic turnover of the elements C, H, O and N under aerobic conditions. The (pseudo) compounds are given in C-moles, i.e. the values for the elemental contents within an organic molecule are relative to 1 C atom.



In order to clearly separate the COD from the N load, all N in the influent is here assumed to be present in the form of NH<sub>3</sub>. The elemental composition of the substrate was derived from the one given by Orhon and Artan (1994) for domestic waste (CH<sub>1.9</sub>O<sub>0.3</sub>N<sub>0.1</sub>), by eliminating NH<sub>3</sub> from the formula. The biomass composition is quite generally valid for many microbial organisms grown under various conditions, as was shown by Roels (1983).

The stoichiometric coefficient for substrate has been chosen as 1, so that the coefficient c equals the yield of biomass on substrate (expressed in C-mol/C-mol). If this yield is known, the other stoichiometric coefficients (a, b, d and e) can be calculated solving the 4 elemental balances. On the other hand, if the oxygen consumption rate and the carbon dioxide production rate are measured, for example, the biomass production rate can be calculated without any assumptions with respect to this yield (see below). In

wastewater treatment, commonly the yield of biomass on substrate for heterotrophs  $Y_H$  is expressed in g-COD X/g-COD S as in the IAWQ model #1 (Henze *et al.*, 1987). To calculate the  $CO_2$  production (which is not covered by the IAWQ model # 1) the biomass yield on a C-mol basis is required and the following relation can be used:

$$c = \frac{COD_S / TOC_S}{COD_X / TOC_X} * Y_H \quad (2)$$

$COD_i$  denotes the COD content of 1 g of compound i and  $TOC_i$  the total (organic) carbon content of compound i (g C/g i). Counting the net number of electrons that can be transferred to oxygen (for one C-mol biomass  $4+1.8-1-0.6=4.2$  and for one C-mol of substrate  $4+1.6-0.6=5$ ), stoichiometric COD values can be calculated as:  $COD_X = 1.37$  g-COD/g X,  $COD_S = 2.15$  g-COD/g S. The TOC values follow directly from the elemental composition:  $TOC_X = 0.488$  g C/g X and  $TOC_S = 0.645$  g C/g S.

If equation 1 is considered to express biomass growth at the maximum growth rate, the often reported yield factor  $Y_H = 0.65$  g-COD X/g-COD S can be used (Henze *et al.*, 1987). This is equivalent to 0.772 C-mol X per C-mol S. Under practical conditions, the growth rate is well below the maximum growth rate, so that the observed yield  $Y_H^{obs}$  is significantly smaller than the maximum value of 0.65.  $Y_H^{obs}$  is the ratio of the measured rates of heterotrophic biomass production and substrate uptake:

$$Y_H^{obs} = \frac{R_{H,X}}{R_{H,S}} = \frac{r_{H,X}}{r_{H,S}} * \frac{COD_X / TOC_X}{COD_S / TOC_S} \quad (3)$$

Here, the capital 'R' is used for reaction rates in mass (g-COD, g N or g  $O_2$ ) per unit time whereas 'r' is in (C-) mol per unit time. In this paper, R and r have positive values for both consumed and produced quantities.  $Y_H^{obs}$  can be expressed as a function of  $Y_H$ , the sludge residence time (SRT), and the decay coefficient  $b_H$  under steady state conditions (see for example Orhon and Artan, 1994):

$$Y_H^{obs} = \frac{Y_H}{1 + (1 - Y_H) * b_H * SRT} \quad (4)$$

Substituting some characteristic values (SRT = 15 d,  $Y_H = 0.65$  g-COD X/g-COD S,  $b_H = 0.4$  d<sup>-1</sup>), the resulting  $Y_H^{obs}$  value is 0.21. So, effectively, 0.21 g-COD living biomass will be produced under these conditions from 1 g-COD substrate (or 0.249 C-mol X/C-mol S). The heterotrophic oxygen consumption  $R_{H,O}$  follows from the COD balance:

$$R_{H,O} = R_{H,S} - R_{H,X} \quad (5)$$

In molar units one can write ( $M_I$  is the weight of one C-mol of compound I):

$$R_{H,O} = M_O * r_{H,O} = M_S * COD_S * r_{H,S} - M_X * COD_X * r_{H,X} \quad (5a)$$

Equation 5a expresses the net uptake of COD, equivalent with grams of molecular oxygen. As 1 C-mol contains by definition 12 g of C,  $M_I$  may be substituted by:

$$M_I = 12/TOC_I \quad (6)$$

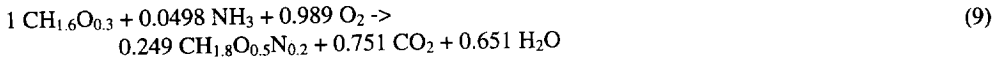
$M_O = 32$ , so that equation 5a may be rewritten as:

$$r_{H,O} = (1 - Y_H^{obs}) * \frac{COD_S}{TOC_S} * r_{H,S} * \frac{12}{32} \quad (7)$$

From the C-balance, the carbon dioxide production rate  $r_{H,C}$  can be calculated:

$$r_{H,C} = r_{H,S} - r_{H,X} = (1 - Y_H^{obs}) * \frac{COD_S / TOC_S}{COD_X / TOC_X} * r_{H,S} \quad (8)$$

The coefficient b from equation 1 equals  $r_{H,O}/r_{H,S}$  and d is  $r_{H,C}/r_{H,S}$ , so that b and d can be calculated from equations 7 and 8; a follows from nitrogen balance and e from the O or H balance:



which represents the stoichiometry for heterotrophic C-conversion under the mentioned characteristic conditions.

Using equations 7 and 8, we can analyse which information  $r_{H,O}$  and  $r_{H,C}$  contain with respect to the heterotrophic C-conversion (if that is the only conversion proceeding). If we assume that  $COD_X/TOC_X$  has a constant value of 2.81 due to the quite constant biomass composition in nature, both equations 7 and 8 can be used to calculate the substrate conversion rate in g-COD S/d. When  $r_{H,S}$  is eliminated from these equations, the ratio  $r_{H,C}/r_{H,O}$  can be used to measure the COD/TOC ratio of the substrate. For the ratio  $r_{H,C}/r_{H,O}$  we will use the term RQ (respiratory coefficient) that is used in fermentation literature (Roels, 1983). The superscripts i and C indicate 'intrinsic value' and 'C-removal' respectively.

$$RQ^{iC} = \frac{r_{H,C}}{r_{H,O}} = \frac{32}{12} * \frac{\left(\frac{COD_S}{TOC_S}\right)^{-1} - \frac{Y_H^{obs}}{2.81}}{1 - Y_H^{obs}} \quad (10)$$

Note that both TOC and COD may be expressed in equation 10 per unit mass (as was done here) or per unit volume which is more common in practice. When the COD/TOC ratio for substrate equals that for biomass, the  $(1 - Y_H^{obs})$  factor cancels from equation 10, and  $RQ^{iC}$  obtains a constant value of 0.95. However, in general, these COD/TOC ratios are not equal (for the  $COD_S/TOC_S$  ratio of 3.33 given above,  $RQ^{iC}$  equals 0.76). Moreover,  $COD_S/TOC_S$  may vary with the wastewater composition. Equation 10 can more conveniently be rewritten as:

$$\left(\frac{COD_S}{TOC_S}\right)^{-1} = \frac{12}{32} * ((1 - Y_H^{obs}) * RQ^{iC} + 0.95 * Y_H^{obs}) \quad (11)$$

Clearly, the reciprocal COD/TOC ratio of the converted substrate is a linear function of the  $RQ^{iC}$  (assuming a constant value for  $Y_H^{obs}$ ). This means that  $RQ^{iC}$  is hardly sensitive to sludge age or decay but is a very strong measure of the COD/TOC ratio of the consumed substrate. Whether this result holds as well under practical conditions with simultaneous nitrification and denitrification will be examined in the next section.

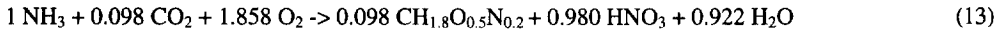
**Biomass production rate.** As mentioned before,  $r_{H,O}$  and  $r_{H,C}$  can be used to calculate the biomass production rate. Using the compounds from equation 9, one obtains, solving the elemental balances:

$$R_{H,X} = 12 * \frac{COD_X}{TOC_X} * (5 * r_{H,O} - 6.25 * r_{H,C}) \quad (12)$$

So, the coefficients in equation 12 depend on the substrate composition (and on the biomass composition), but not on the yield  $Y_H^{obs}$ . The substrate composition can be calculated from COD<sub>S</sub> and TOC<sub>S</sub> data.

### Nitrification

The biologically produced CO<sub>2</sub> is used to calculate the intrinsic RQ<sup>i</sup>. In practice, the bicarbonate/CO<sub>2</sub> equilibrium can consume or produce CO<sub>2</sub> depending on pH and H<sup>+</sup> producing or consuming reactions like nitrification. Therefore, there is a complex relation between measured CO<sub>2</sub>, HCO<sub>3</sub><sup>-</sup> and pH. To estimate the contribution of nitrification to oxygen consumption and carbon dioxide production/consumption, we consider complete N-oxidation to NO<sub>3</sub><sup>-</sup> by chemo-autotrophic bacteria (Orhon *et al.*, 1994), using a yield value  $Y_A$  for autotrophs on nitrate-N of 0.24 g-COD X/g NO<sub>3</sub>-N (Henze *et al.*, 1987):



Contrary to heterotrophic growth, the dependence of observed yields on biomass decay and/or sludge age will not be addressed here, as equation 13 indicates that only 2% of the nitrogen is transferred to biomass. Moreover, the autotrophic decay coefficient and biomass concentration are low compared with heterotrophic biomass ( $b_A X_A$  is typically 25-50 times lower than  $b_H X_H$ ), so that the turnover of CO<sub>2</sub> via autotrophic biomass to heterotrophic biomass can be neglected here as well. The following relations for the conversion rates of oxygen ( $r_{A,O}$ ) and carbon dioxide ( $r_{A,C}$ ) can be derived:

$$r_{A,O} = \frac{1}{32} * \frac{4.57 - Y_A}{i_B Y_A + 1} * R_{A,N} \quad (14)$$

$$r_{A,C} = \frac{1}{M_X \text{COD}_X} * \frac{Y_A}{i_B Y_A + 1} * R_{A,N} \quad (15)$$

where  $i_B$  is the N content of the biomass (g N/g COD). The intrinsic RQ<sup>i,N</sup> value for nitrification then reads:

$$\text{RQ}^{i,N} = \frac{-r_{A,C}}{r_{A,O}} = \frac{32}{M_X \text{COD}_X} * \frac{Y_A}{Y_A - 4.57} \quad (16)$$

For the parameter values used before, the RQ<sup>i,N</sup> equals -0.053, which is quite different from typical RQ<sup>i,C</sup> values in the range 0.7-1.0.

### Denitrification

In the heterotrophic denitrification process, NO<sub>3</sub><sup>-</sup>/NO<sub>2</sub><sup>-</sup> is used as electron acceptor instead of oxygen. Here only NO<sub>3</sub><sup>-</sup> is considered that is assumed to be used exclusively in dissimilation (biomass-N is provided by ammonia). We will follow here the approach of the IAWQ model #1, where the oxic yield for heterotrophs is used for anoxic conversion as well, so that at the level of electron transfer, the anoxic and oxic processes are equivalent. Hence, the nitrate consumption under anoxic conditions is calculated stoichiometrically from the oxygen consumption under oxic conditions (equation 8). As 1 molecule of NO<sub>3</sub><sup>-</sup> can accept 5 electrons, the following equation is obtained for nitrate consumption:

$$r_{D,NO} = (1 - Y_H^{obs}) * \frac{\text{COD}_S}{\text{TOC}_S} * r_{D,S} * \frac{12}{32} * \frac{4}{5} \quad (17)$$

For the CO<sub>2</sub> production rate equation 8 can be used again.

OBSERVATIONS FROM GAS PHASE CO<sub>2</sub> AND O<sub>2</sub> MEASUREMENTS

Here, the measurable gas phase CO<sub>2</sub> and O<sub>2</sub> concentrations will be related to the conversion rates  $r_{H_2O}$ ,  $r_{H_2C}$ ,  $r_{A,O}$  and  $r_{A,C}$ . With respect to CO<sub>2</sub>, calculations are not straightforward, due to the equilibrium between CO<sub>2</sub> and bicarbonate (HCO<sub>3</sub><sup>-</sup>) (which is the predominant CO<sub>2</sub> involved reaction at the typical pH range of 6.5-8):



In the subsequent calculations, we assume that bicarbonate is the only buffering agent and NH<sub>4</sub><sup>+</sup> is the only soluble N-compound. This implies that the CO<sub>2</sub> in the gas phase depends not only on the produced CO<sub>2</sub>, but also on the pH and on the H<sup>+</sup> production that equals the bicarbonate consumption ( $r_{H,B}$  for heterotrophs and  $r_{A,B}$  for autotrophs). These bicarbonate conversions can be derived from equations 1 and 13, if bicarbonate and charge are included. The net CO<sub>2</sub> conversion rate then follows from:

$$r_C = r_{H,C} + r_{H,N} - r_{A,C} + 2^*r_{A,NO} = r_{H,C} + r_{H,B} - r_{A,C} + r_{A,B} \quad (19)$$

If denitrification proceeds as well, one proton is consumed for each oxidised N atom, so that an extra term is added to equation 19:

$$r_C = r_{H,C} + r_{H,B} - r_{A,C} + r_{A,B} - r_{D,NO} \quad (19a)$$

From the bicarbonate and the CO<sub>2</sub> balances, the liquid CO<sub>2</sub> and HCO<sub>3</sub><sup>-</sup> concentrations can be calculated. Next, the equilibrium equation belonging to the reaction of equation 18 can be used to calculate the pH resulting from these concentrations:

$$pH = -\log(H) = -\log\left(\frac{K_B * C}{B}\right) \quad (20)$$

For  $pK_B$  ( $-\log K_B$ ) a value of 6.38 (at 20°C) is reported (Weast, 1989), so that, for example, at pH 7, 80% of the dissolved carbon dioxide is present in the form of bicarbonate.

Simulation model

For the subsequent calculations we will consider a continuous stirred tank reactor (CSTR) in which the heterotrophic and autotrophic turnover proceed simultaneously. The reactor is assumed to be in steady state and to be perfectly mixed with regard to the liquid and the gas phase. The contribution of liquid phase transport to the oxygen balance is neglected.

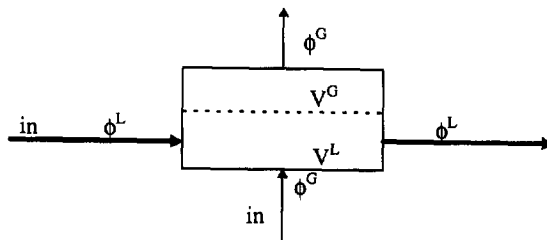


Figure 1. The CSTR one reactor model.

**Liquid phase balance equations**

$$\text{carbon dioxide } \phi^L/V^L (C_{in}^L - C^L) = -r_C + \phi_C^{L \rightarrow G} \quad (21)$$

$$\text{bicarbonate } \phi^L/V^L (B_{in}^L - B^L) = r_{H,B} + r_{A,B} (-r_{D,NO}) \quad (22)$$

$$\text{substrate } \phi^L/V^L (S_{in}^L - S^L) = r_{H,S} \quad (23)$$

$$\text{ammonium } \phi^L/V^L (N_{in}^L - N^L) = r_{H,N} + r_{A,N} \quad (24)$$

$$\text{nitrate } \phi^L/V^L (NO_{in}^L - NO^L) = -r_{A,NO} (+ r_{D,NO}) \quad (25)$$

$$\text{oxygen } \phi^L/V^L (O_{in}^L - O^L) = r_{H,O} + r_{A,O} (-r_{D,NO} * 5/4) - \phi_O^{G \rightarrow L} \quad (26)$$

**Gas phase balance equations**

$$\text{carbon dioxide } \phi^G (C_{in}^G - C^G) = -\phi_C^{L \rightarrow G} \quad (27)$$

$$\text{oxygen } \phi^G (O_{in}^G - O^G) = \phi_O^{L \rightarrow G} \quad (28)$$

**Inter phase transport equations**

$$\text{oxygen transfer } \phi_O^{G \rightarrow L} = (k_{L,a})_O * (O^G/H_O - O^L) \quad (29)$$

$$\text{carbon dioxide transfer } \phi_C^{L \rightarrow G} = (k_{L,a})_C * (C^L - C^G/H_C) \quad (30)$$

**Thermodynamics**

$$\text{Bicarbonate equilibrium } K_B = H * B / C \quad (31)$$

**Respiratory coefficients**

$$\text{Gas phase measurable RQ } RQ^G = (C^G - C_{in}^G)/(O_{in}^G - O^G) \quad (32)$$

$$\text{Intrinsic RQ } RQ^i = r_C / (r_{H,O} + r_{A,O}) \quad (33)$$

**Parameter values.** The dimensions of the reactor and flows are characteristic for a 120,000 population equivalent sized plant. The gas flow rate ( $\phi^G$ ) was determined separately for each simulation run, so that the liquid oxygen concentration was kept at 1.5 g/m<sup>3</sup>, which is here approximately equivalent to a gas phase oxygen depletion of 10%. Table 1 contains all other parameter values.

Table 1. Values used in the simulations (20°C)

par.	value	units	par.	value	units
$B_{in}^L$	$4 + N_{in}^L$ <sup>1)</sup>	mol/m <sup>3</sup>	$H_o$	32 <sub>3)</sub>	mol/mol
$N^L$	0 <sup>2)</sup>	g N/m <sup>3</sup>	$H_C$	1.08 <sub>3)</sub>	mol/mol
$S^L$	0 <sup>2)</sup>	g-COD/m <sup>3</sup>	$k_{L,aO}$	200	d <sup>-1</sup>
$NO_{in}^L$	0	g N/m <sup>3</sup>	$k_{L,aC}$	$0.83 * k_{L,aO}$ <sup>4)</sup>	d <sup>-1</sup>
$O_{in}^L$	0	mol/m <sup>3</sup>	$V_L$	12000	m <sup>3</sup>
$C_{in}^L$	0.76	mol/m <sup>3</sup>	$\phi^L$	24000	m <sup>3</sup> /d
$O_{in}^G$	8.792	mol/m <sup>3</sup>	$Y_H^{obs}$	0.21	g-COD/g-COD
$C_{in}^G$	0,0125	mol/m <sup>3</sup>	$Y_A$	0.24	g-COD/g NO <sub>3</sub> -N
$K_B$	$4.17 * 10^{-4}$	mol/m <sup>3</sup>			

1. The bicarbonate concentration in the influent ( $B_{in}^L$ ) is assumed to be the sum of a constant value of 4 mol/m<sup>3</sup> - a common value for tap water in the Netherlands (van Helvoort *et al.*, 1992) - and 1 mol HCO<sub>3</sub><sup>-</sup> per mol NH<sub>4</sub><sup>+</sup> in the influent.

2. The reactor, hence effluent, concentrations for substrate and nitrogen are set to zero. In doing so, the influent load of NH<sub>4</sub><sup>+</sup> and substrate can be regarded as the converted amounts in a practical situation.

3. Note that the Henry coefficients - relating the liquid to gas phase concentrations in equilibrium (eq. 29 and 30) - are given here for both gas and liquid phase concentrations in mol/m<sup>3</sup>.

4. This relation follows from the penetration film theory that states that the ratio of two  $k_{L,a}$  values for two different substances equals the square root of the ratio of the diffusion coefficients of those substances.  $\sqrt{(D_C/D_O)} = 0.83$  (Noorman *et al.*, 1994).

## RESULTS AND DISCUSSION

C-removal and nitrification

Table 2 shows the simulation results for simultaneous C-removal and nitrification for various C- and N-oxidation rates. The denitrification terms in equations 22, 25 and 26 were set to zero for these calculations. The  $COD_S/TOC_S$  ratio was 3.33 in these calculations. Removed COD was varied between 400, 600 and 800 g-COD/m<sup>3</sup>. Per COD value three levels for removed nitrogen were applied: the minimum amount required for heterotrophic biomass formation, 25 and 50 g N/m<sup>3</sup>. Higher nitrogen concentrations than 50 g/m<sup>3</sup> would have lead to an unacceptable pH drop due to the absence of denitrification.

*Ratio of C-removal to nitrification.* It is clear from the calculations that the intrinsic  $RQ^i$  is rather sensitive to the ratio of C-removal to nitrification. The easily measurable  $RQ^G$  however, is not. Due to the extra production of CO<sub>2</sub> from bicarbonate, the effect of nitrification on  $RQ^G$  is relatively small.

Table 2. Simulation results for simultaneous C-removal and nitrification

$S_{in}^L$ g-COD/m <sup>3</sup>	$N_{in}^L$ g N/m <sup>3</sup>	$B_{in}^L$ mol/m <sup>3</sup>	pH	$\phi^G$ m <sup>3</sup> /d	CO <sub>2</sub> <sup>G</sup> mol/m <sup>3</sup>	$RQ^G$ -	$RQ^i$ -	CO <sub>2</sub> <sup>L</sup> mol/m <sup>3</sup>	B <sup>L</sup> mol/m <sup>3</sup>	$\phi_{\pi C}^G/\phi_{\pi C}^L$ -
400	7	4.50*	6.99	212880	0.872	0.768	0.759	0.981	4.00	1.55
	25	5.79	6.82	284400	0.860	0.816	0.601	0.984	2.74	2.74
	50	7.57	6.39	392400	0.833	0.859	0.462	0.971	0.99	6.95
600	10.5	4.75*	7.03	367200	0.777	0.788	0.759	0.903	4.00	2.43
	25	5.79	6.90	432240	0.770	0.813	0.666	0.904	2.98	3.57
	50	7.57	6.52	552000	0.752	0.847	0.547	0.897	1.23	8.12
800	14	5.00*	7.05	541200	0.711	0.796	0.759	0.847	4.00	3.31
	25	5.79	6.96	595800	0.707	0.811	0.704	0.847	3.23	4.30
	50	7.57	6.62	726600	0.693	0.838	0.601	0.842	1.48	9.04

\* Heterotrophic C-removal only.

The last column of table 2 indicates the ratio of inorganic carbon in exhaust gas relative to the inorganic carbon in the liquid outflow. This ratio appears to increase significantly with increasing nitrification. The gas phase concentration however remains rather constant, as the gas flow rate must be increased to maintain the DO level at about 1.5 mg/l. The most sensitive measure for nitrification of the variables considered in table 2 is the alkalinity difference of plant influent and effluent. The effluent bicarbonate concentration can be estimated from the CO<sub>2</sub> gas measurements in combination with pH measurements with equation 31 with an accuracy of probably 10-15%. However, the influent alkalinity must be known as well, so that measurements are inevitable. These tests are relatively simple, and recently an automatic detection method has been described (Guwy *et al.*, 1994).

*COD<sub>S</sub>/TOC<sub>S</sub> ratio.* In table 2, data are shown for one  $COD_S/TOC_S$  ratio. Calculations for other ratios showed that  $RQ^G$  is still much more sensitive to this ratio than to the substrate  $COD_S/NS$  ratio. This is also true for combined nitrification/denitrification and will be shown below.

*Biomass production rate.* If nitrification activity is quantified via alkalinity measurements, or with direct ammonia measurements, the intrinsic oxygen uptake rate and the carbon dioxide production rate can be calculated if the gas flow rate is measured in addition. This means that the biomass production rate can (on-line) be estimated via the elemental balances, similarly to equation 12. It should be noted though, that accurate gas flow measurements are more difficult to perform than the concentration measurements of CO<sub>2</sub> and O<sub>2</sub>.



*Total oxidation activity.* The combination of gas flow rates with the concentration difference of oxygen in the inlet and exhaust air gives the oxygen uptake rate by the plant, which of course is a direct measure for combined C-removal and nitrification. At higher nitrogen loads, loss of nitrification can be indicated directly, though not quantitatively, from this oxygen transfer rate. It should be stressed that this is a powerful on-line measurement that indicates oxidation activity more directly and more accurately than, for example, respirometry. Changes in the load of the plant are immediately monitored. When combined with dissolved oxygen measurements,  $k_L a$  values can be estimated as well that can indicate sudden changes in the influent composition (Howell *et al.*, 1985).

### C-removal, nitrification and denitrification

Figure 2 presents the measurable  $RQ^G$  values when in the same reactor complete denitrification is assumed to occur simultaneously. The  $RQ^G$  values are plotted here as a function of both the COD/N ratio (at an influent substrate concentration of 800g-COD/m<sup>3</sup>) and the COD/TOC ratio. The range was chosen on the basis of the work of Rao (1978), who reported COD/TOC ratios of 2.5 (in the effluent of a brewery treatment plant) up to 4.98 (influent of the Louvain-La-Neuve municipal wastewater treatment plant). Simultaneous denitrification is of course a simplification in the sense, that practically, wastewater will be exposed to anoxic conditions to obtain substantial denitrification. However, it can be argued that gas measurements in a subsequent aerated process section should reveal comparable results.

*Ratio of C- to N-removal.* Denitrification causes additional alkalinity production (i.e. reduced CO<sub>2</sub> production) and reduced oxygen consumption. Here, the alkalinity consumption is exactly balanced by the sum of alkalinity production by ammonification (which is accounted for in the  $B_{in}^L$  values) and by denitrification, so that the alkalinity of the effluent is in all cases 4 mol/m<sup>3</sup>. The  $RQ^G$  values with and without denitrification turn out to be hardly different. For example, at an influent concentration of 800 g-COD/m<sup>3</sup> substrate and 50 g NH<sub>3</sub>-N/m<sup>3</sup>, the total CO<sub>2</sub> production rate is calculated at 5.00 x 10<sup>4</sup> mol/d for C-removal and nitrification, and at 4.40 x 10<sup>4</sup> mol/d with concurrent denitrification. The oxygen uptake rates are for both situations respectively 5.89 x 10<sup>4</sup> mol/d and 5.13 x 10<sup>4</sup> mol/d.  $RQ^i$  values based on these numbers are 0.850 and 0.857 respectively. The calculated  $RQ^G$  values are about the same (0.838 and 0.842).

Bicarbonate measurements are less sensitive than in the previous case without denitrification, because of the constant effluent concentration. (Note that the influent alkalinity may be lower in practice, because ammonification will proceed partly in the plant). Over the whole range of influent COD<sub>S</sub> and N<sub>S</sub> values, the measured  $RQ^G$  values are here only slightly more sensitive for the C<sub>S</sub>/N<sub>S</sub> ratio of the converted substrate. Even moderate changes (10-20 g/m<sup>3</sup>) in the N-content of the influent can hardly be monitored from the  $RQ^G$ . Only a substantial loss of nitrification at high nitrogen levels can be signalled. Loss of denitrification can be monitored via alkalinity measurements.

*COD<sub>S</sub>/TOC<sub>S</sub> ratio.* Figure 2 shows clearly that the  $RQ^G$  is very sensitive to the COD<sub>S</sub>/TOC<sub>S</sub> ratio of the converted substrate and, as stated above, hardly to the COD<sub>S</sub>/N<sub>S</sub> ratio, especially at lower to moderate COD<sub>S</sub>/N<sub>S</sub> ratios. In addition, it was shown above that also sludge age and/or decay hardly influence the  $RQ^G$  value. This means that it seems feasible to use  $RQ^G$  measurements for determining on-line COD<sub>S</sub>/TOC<sub>S</sub> ratios, hence to replace the laborious COD<sub>S</sub> measurements with  $RQ^G$  and TOC<sub>S</sub> measurements. It is stressed again that  $RQ^G$  measurements only require O<sub>2</sub> and CO<sub>2</sub> measurements in the off-gas and not gas flow measurements.

Probably a more or less linear relation exists between the reciprocal substrate COD<sub>S</sub>/TOC<sub>S</sub> value and the  $RQ^G$  (see equation 10). This conclusion holds as well for the combination of C-removal and N-removal (results not shown here). Practical experiments are in progress to verify this finding and analyse the practically feasible accuracies and the influence of plant and influent dynamics.

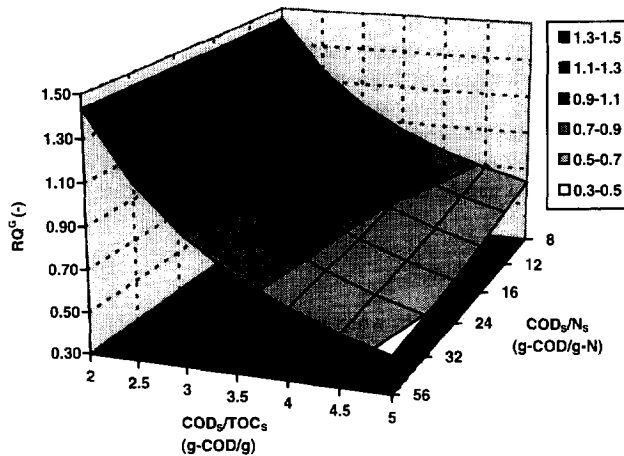


Figure 2. Intrinsic  $RQ^i$  values for simultaneous C-removal, nitrification and denitrification for an influent concentration of  $800 \text{ g-COD/m}^3$ .

### NOMENCLATURE

b	decay coefficient	$\text{d}^{-1}$
B	bicarbonate concentration	$\text{mol m}^{-3}$
C	carbon dioxide concentration	$\text{mol m}^{-3}$
$\text{COD}_I$	chemical oxygen demand for compound I	$\text{g-O}_2 (\text{g I})^{-1}$
CPR	$\text{CO}_2$ production rate	$\text{mol d}^{-1}$
D	diffusion coefficient	$\text{m}^2 \text{s}^{-1}$
H	proton concentration	$\text{mol m}^{-3}$
$H_{\text{O}_2}$	Henry coefficient for $\text{O}_2$	$\text{mol mol}^{-1}$
$H_{\text{C}}$	Henry coefficient for $\text{CO}_2$	$\text{mol mol}^{-1}$
$i_{\text{B}}$	nitrogen content of biomass	$\text{g-N (g-COD X)}^{-1}$
$K_{\text{B}}$	$\text{CO}_2/\text{HCO}_3^-$ equilibrium constant	$\text{mol m}^{-3}$
$k_{\text{La}}$	volumetric mass transfer coefficient	$\text{d}^{-1}$
M	(C-)molar mass	$\text{g (C-)mol}^{-1}$
N	ammonia/ammonium concentration	$\text{mol m}^{-3}$
O	$\text{O}_2$ concentration	$\text{mol m}^{-3}$
OUR	$\text{O}_2$ uptake rate	$\text{mol d}^{-1}$
R	conversion rate	$\text{g m}^{-3} \text{d}^{-1}$
r	conversion rate	$\text{mol m}^{-3} \text{d}^{-1}$
RQ	respiratory coefficient	$\text{mol mol}^{-1}$
S	substrate concentration	$\text{g-COD d}^{-1}$
SRT	sludge residence time	d
$\text{TOC}_I$	total organic carbon of compound I	$\text{g-C (g I)}^{-1}$
V	volume	$\text{m}^3$
X	biomass concentration	$\text{g-COD m}^{-3}$
Y	yield	$\text{g g}^{-1}$

### Greek

$\phi$	flow rate	$\text{m}^3 \text{d}^{-1}$
$\phi_{\text{O}}^{\text{G} \rightarrow \text{L}}$	gas to liquid $\text{O}_2$ flow	$\text{mol m}^{-3} \text{d}^{-1}$
$\phi_{\text{C}}^{\text{L} \rightarrow \text{G}}$	liquid to gas $\text{CO}_2$ flow	$\text{mol m}^{-3} \text{d}^{-1}$

### Subscripts

A	autotrophic
B	bicarbonate
C	carbon dioxide
H	heterotrophic
in	influent
N	ammonia/ammonium
NO	nitrate
O	oxygen
S	substrate
TIC	total inorganic carbon

### Superscripts

i	intrinsic
C	C-removal
G	gas phase
L	liquid phase
N	nitrification
obs	observed

## CONCLUSION

The simulations show that exhaust gas phase concentration measurements of CO<sub>2</sub> and O<sub>2</sub> can be used for various purposes. These measurements are sufficient to calculate an observed respiratory coefficient (RQ<sup>G</sup>) that is primarily indicative of the COD/TOC ratio of the converted substrate. This conclusion holds for C-removal, whether or not combined with N-removal (nitrification and/or denitrification). These gas phase measurements are not sufficient to monitor N-removal versus C-removal (although a severe loss of nitrification at high N-loads can be observed). If oxygen measurements are combined with gas flow measurements, (rapid changes in) overall oxidation activity can be monitored on-line as well as k<sub>L</sub>a values (in combination with dissolved oxygen probes). If N-removal is determined in a different way (and maybe alkalinity tests are sufficient for that, especially if no denitrification is present), biomass production can be estimated on-line using these gas measurements, which may be beneficial for sludge level control.

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