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FULL-SCALE ON-LINE ASSESSMENT OF TOXIC WASTEWATERS CAUSING CHANGE IN BIODEGRADATION MODEL STRUCTURE AND PARAMETERS

Peter A. Vanrolleghem*, Zaide Kong** and Filip Coen*

** BIOMATH, University of Gent, Coupure Links 653, B-9000 Gent, Belgium*
*** Centre for Environmental Sanitation, University of Gent, Coupure Links 653, B-9000 Gent, Belgium*

ABSTRACT

Detecting wastewater toxicity in due time is essential for protection of a sewage works and the receiving waters. A respirometric method is presented that performs short batch experiments, so-called In-Sensor-Experiments for toxicity detection. Two types of wastewater samples can be added to the reactor in the device: either the potentially toxic wastewater entering the plant, or, a defined mixture of acetate and ammonia. From the latter experiments models are identified that describe the heterotrophic and autotrophic activity of the sludge. Since these 'calibration' experiments are alternated with experiments in which wastewater is injected, the effect of the wastewater on the sludge can be quantified unequivocally.

Full-scale toxicity detection (and the corresponding effluent quality) results are reported for a plant treating a mixture of hospital and municipal wastewaters. The respirometer was installed at the influent line of the plant. It was evaluated during a 6-month period for its on-line toxicity detection capacity. Both deliberate and accidental intoxications were recorded and compared with off-line toxicity measurements. Inhibitory wastewaters affected the nitrification activity of the sludge. This was confirmed by the concomitant increase in NH_4^+ discharge of the treatment plant. To evaluate the efficiency of control actions, the deliberate addition of toxicant was interrupted at the time a toxicity alarm was triggered by the respirometer. It was observed that plant performance then remained unaffected for all monitored criteria. Copyright © 1996 IAWQ. Published by Elsevier Science Ltd

KEYWORDS

Mathematical modelling; model selection; respirometry; sensors; toxicity; wastewater treatment.

INTRODUCTION

On-line evaluation of wastewater toxicity is a prerequisite for protection of treatment plants from inhibitory influents. Although one is aware of the magnitude of the problem -especially in industry, very few full-scale results are available on (1) monitoring equipment capable to predict the potential toxicity of an influent or (2) control strategies that have proved successful in the protection of sewage works. Often, only an a posteriori assessment is made of what has caused a plant upset. Before turning the attention to the toxicity monitoring equipment and detection principles which were evaluated in this study, it is good to shortly review the goals of toxicity detection and the actions one can take at a treatment plant if a toxic influent is

detected. It is evident that the goal of a treatment plant is to maintain the receiving water quality. If inhibitory substances enter the treatment plant, the receiving water is endangered due to

(1) direct (acute) toxic effects if the toxicant is not eliminated in the plant and is discharged, but also
(2) indirect (chronic) effects due to collapse of the biodegradative capacity of the plant because of the death of (part of) the microbial population. Increased organic and nutrient levels in the effluent may result, possibly for a longer time as start-up may be necessary.

Let's now consider a few possible protective actions:

(1) Often a bypass line is available by which influent can be diverted directly to the receiving waters.
(2) Some form of sludge storage may be present at the sewage works. Step feed operation can be regarded as a particular case where aeration tanks are used for temporary storage of sludge
(3) In many industrial treatment plant designs calamity basins have been included allowing to divert a certain volume of a potentially toxic wastewater (Vanrolleghem *et al.*, 1994a).

Table 1. Effect of protective control actions on receiving water quality

Control Action	Toxicant Eliminated by Sludge	Acute Toxic Effect on		Chronic Pollution Effect on Receiving Water
		Sludge	Receiving Water	
None	Yes	Yes	No	Yes
	No	Yes	Yes	Yes
Bypass	NA*	No	Yes	No
Partial Sludge Storage	Yes	Partial	No	Partial
	No	Partial	Yes	Partial
Calamity Basin	NA*	No	No	No

*NA: Not applicable

In Table 1, an evaluation is made of these control actions with respect to the short- and long-term effect on the receiving water quality. It should be obvious that the calamity basin option is clearly the best as it allows one to protect both the treatment plant and the receiving water. However, if this protective measure is not available or the discharged toxic pulse is too voluminous, a trade-off must be sought between the short-term effects caused by breakthrough of toxicants and the long-term pollution effects.

The decisions to be made, however, depend on the type of interaction between the inhibitory agents and the activated sludge. Activated sludge may act as a physicochemical adsorbent or it may (partially) biodegrade the toxicants. Although important efforts are being made, the fate of toxicants in activated sludge systems is clearly insufficiently understood to support such decisions. In any case, the full potential of dedicated equipment for protection of treatment plants will only be useful when the actuators are manipulated in due time on the basis of adequate information. First of all, it is essential to detect the presence of toxicants in a wastewater. Subsequently, analyses should be performed to predict the fate of the toxicant in the treatment plant in view of the effects given in Table 1.

On-line detection of toxicity to biological wastewater treatment plants mainly relies on respirometric techniques since the devices are easy to operate, need minimum maintenance costs and give fast and relevant response. The detection principle is based on the monitoring of the sludge exogenous and endogenous respiration rate. Several respiration rate measurement techniques have been implemented (Arthur *et al.*, 1991; Temmink *et al.*, 1993; Watts and Garber, 1993; Vanrolleghem *et al.*, 1994a) and have resulted in several commercially available on-line toximeters. The published reports showed their capacities to detect toxic shock loadings either in the lab or in a lab scale pilot plant. In the past, however, no long-term

experiments have been reported that check or verify the reliability of such apparatus for on-line toxicity control at a full-scale wastewater plant. The aim of this study was therefore to investigate the performance of such a toximeter, *in casu* the RODTOX, on a full-scale wastewater treatment plant.

The RODTOX (Rapid Oxygen Demand and TOXicity Tester) is an open respirometric biosensor for rapid determination of both organic load and potential toxicity of wastewater to the treatment plant. Previous studies showed that it can be used for the following purposes:

(1) On-line BOD and toxicity detection (Vanrolleghem *et al.*, 1994a)
(2) Off-line IC50 estimation of a chemical (Kong *et al.*, 1993)
(3) Off-line respiration inhibition kinetics analysis (Kong *et al.*, 1994a)

This paper presents results obtained during a long-term reliability test of this respirometer for both short-term BOD (stBOD) determination and toxicity detection at full-scale. The 6 months experiment was designed in two phases. During the first three months, the normal performance of the plant was monitored systematically and the stBOD measurements were evaluated (see Kong *et al.*, 1994b). Secondly, the instruments' reliability for toxicity detection was tested by deliberate intoxication using the broad spectrum phenolic disinfectant creoline. Two means of data interpretation were used for toxicity detection. The traditional method is reported elsewhere (Kong *et al.*, 1994b). Here, a new model-based approach giving more detailed toxicity information is introduced. It is based on the evaluation of a change in biodegradation kinetics using respirometric data obtained from In-Sensor-Experiments in which the effect of a potentially toxic influent on activated sludge is characterized in terms of a biodegradation model.

The purpose of the experiments was to see whether a toxicity detection can be made in due time to protect the plant. The toxicity of the wastewater was also monitored off-line with the Microtox measurement.

MATERIALS AND METHODS

Description of the respirometric biosensor

Hardware. The RODTOX biosensor (commercially available from KELMA bvba, Niel, Belgium) consists of a biological system, peripheral equipment, and an electronic component (microprocessor with operating software) that interfaces the first two (Fig. 2, right). The biological component is a reactor vessel, filled with 10 l of activated sludge taken from the wastewater treatment plant at which the device is installed. The mixed liquor is subject to constant aeration (15 l/min); it is also stirred and thermostated. Wastewaters and calibration substrates are introduced with precision membrane pumps (sample volume ranges from 2 to 500 ml). Wastewaters are supplied through a fast loop. A coarse (0.5 mm) tangential filter in this fast-loop bypass line protects the pumping system from clogging. Dissolved oxygen (DO) and pH-electrodes are installed in the cover of the bioreactor. The DO-data are collected and constantly analyzed by the RODTOX microprocessor with the built-in operating software. Advanced data interpretation is conducted with the MOSIFIT software for on-line model identification which is running on the supervising PC.

Operating conditions. The calibration substrate used in the experiments was a multi-substrate solution containing 20 g COD (equimolar HAc and NaAc) and 2 g NH_4^+-N per litre. The calibration volume was 14 ml. The volume of wastewater sample was automatically adjusted by the operating software to 500 ml. Reactor temperature was kept constant at 20°C. The sludge in the RODTOX reactor was renewed every 2 weeks with fresh sludge taken from the treatment plant. The RODTOX was run in automatic mode.

Measurement principle and traditional data interpretation. When the activated sludge in the RODTOX reactor is in the endogenous phase, i.e. when the DO is at the baseline concentration (SOe), a pulse of sample (either calibration substrate or wastewater) is injected (Fig. 1). As a result the activated sludge will increase its exogenous oxygen uptake rate (OUR_{ex}) until the substrate is oxidized completely (which typically takes 30 min). The DO profile (respirogram) is recorded. Traditionally (Vanrolleghem *et al.*,

1994a), the RODTOX calculates three respirometric parameters, i.e. the maximal peak slope (PS) taken from the descending part of the respirogram, peak height (PH) and peak area (PA). Based on the knowledge of the stBOD content of the calibration solution, the sample stBOD can be derived using PH or PA in the following formula:

$$stBOD_{Sample} = \frac{PA(H)_{Sample}}{PA(H)_{Calibration}} stBOD_{Calibration} \quad (1)$$

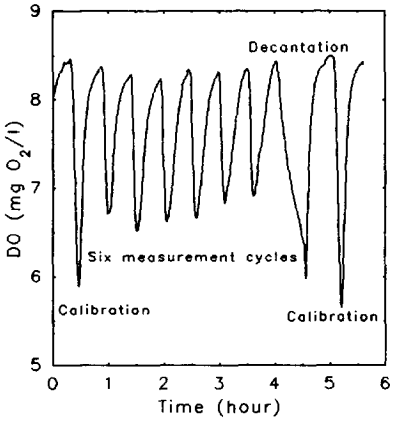

Figure 1. Typical operating sequence of the RODTOX in automatic mode.

The detection of wastewater toxicity towards the activated sludge in the biosensor is based on a comparison of the respirometric parameters of calibration respirograms before (t_1) and after (t_2) the addition of the potentially toxic wastewater sample. The % inhibition of the peak slope, peak height and peak area can be calculated using:

$$\%\,Inhibition = \frac{PS(H,A)_{Calibration}(t_1) - PS(H,A)_{Calibration}(t_2)}{PS(H,A)_{Calibration}(t_1)} 100 \quad (2)$$

Subsequently, these inhibition percentages are evaluated against preset limits and the results used to activate alarm signals. However, the deduction of inhibition is rather heuristic and it was felt that a more mechanistic (model) based approach would allow one to indicate the effective inhibitory action.

Advanced interpretation. The oxygen mass balance in the aerated batch reactor of the respirometric biosensor can be written as:

$$\frac{dS_O}{dt} = K_L a\,(S_O^{sat} - S_O) - OUR_{ex} - OUR_{end} \quad (3)$$

Here, OUR_{ex} represents the exogenous, i.e. substrate induced oxygen uptake rate only. Because the experiments considered for toxicity detection are the regularly performed calibration cycles only, a relatively simple model can be used to describe the measured oxygen dynamics.

Table 2. Process model used for activated sludge characterization (Vanrolleghem and Verstraete, 1993).

Component → / Process ↓	S_S	S_N	X_H	X_A	S_O	Process Rate
Heterotrophic Growth	$-\frac{1}{Y_H}$	$-i_{XB}$	1		$\frac{-(1-Y_H)}{Y_H}$	$\mu_{maxH}\frac{S_S}{K_{mH}+S_S}X_H$
Heterotrophic Decay			-1		$-(1-f_I)$	$b_H X_H$
Autotrophic Growth		$-i_{XB}-\frac{1}{Y_A}$		1	$\frac{-(4.57-Y_A)}{Y_A}$	$\mu_{maxA}\frac{S_N}{K_{mA}+S_N}X_A$
Autotrophic Decay				-1	$-(1-f_I)$	$b_A X_A$

Indeed, the OUR_{ex} in these experiments is determined by the heterotrophic and autotrophic growth on acetate and ammonia respectively. The process kinetics are assumed to be adequately described by the stoichiometry and biodegradation kinetics summarized in Table 2. The oxygen consumption due to both decay processes is put into the endogenous respiration OUR_{end}. As for our purposes endogenous respiration is not considered important and assumed constant, one can rewrite the oxygen balance (Vanrolleghem *et al.*, 1994a):

$$\frac{dS_O}{dt} = K_L a\,(S_O^e - S_O) - OUR_{ex} \tag{4}$$

where the equilibrium or baseline DO is defined by:

$$S_O^e = S_O^{sat} - \frac{OUR_{end}}{K_L a} \tag{5}$$

The aim now is to identify a model describing the biological response after injection of the two-substrate calibration solution. Both the most appropriate model structure and the parameters must be assessed.

For the model structure selection, two candidate structures are available: a Double Monod model in which both substrates are degraded and a Single Monod model where only one of them is oxidized. Model selection methods applied are described in Vanrolleghem *et al.* (1994b).

The given model structures contain a number of unknown parameters such as Y_i, $\mu_{max,i}$, X_i, i_{XB}, f_I, b_i, $K_{m,i}$ and the initial substrate concentrations $S_i(0)$. Not all of these can or have been estimated. The parameters involved in the endogenous respiration (f_I, b_i) for instance, are not involved in eqn (4). For i_{XB} a value of 0.086 g N/g COD was assumed. For the other parameters, it has been shown that only certain combinations are identifiable from OUR_{ex} data (Dochain *et al.*, 1995):

$$\theta_1 = \frac{\mu_{maxH}(1 - Y_H)X_H}{Y_H} \qquad \theta_2 = (1 - Y_H)S_S(0) \qquad \theta_3 = (1 - Y_H)K_{mH} \tag{6}$$

$$\theta_4 = \frac{\mu_{maxA}(4.57 - Y_A)X_A}{Y_A} \qquad \theta_5 = (4.57 - Y_A)S_N(0) \qquad \theta_6 = (4.57 - Y_A)K_{mA}$$

Together with the mass transfer coefficients (K_La, S_O^e), this completes the set of parameters estimated from the DO-data.

Experimental set-up

Evaluation of the method was carried out at the treatment plant of the hospital Maria Middelares (Gent, Belgium). This plant treats a mixture of hospital and domestic wastewater. The works is schematized in Fig. 2 (left). The daily flow is about 230 m^3. The wastewater is pumped to the distribution box (0.5 m^3) and flows through the two aeration tanks (2 x 190 m^3) after passing the screen. The RODTOX sample pump was connected to the influent line of the plant through a fast-loop and a submerged pump.

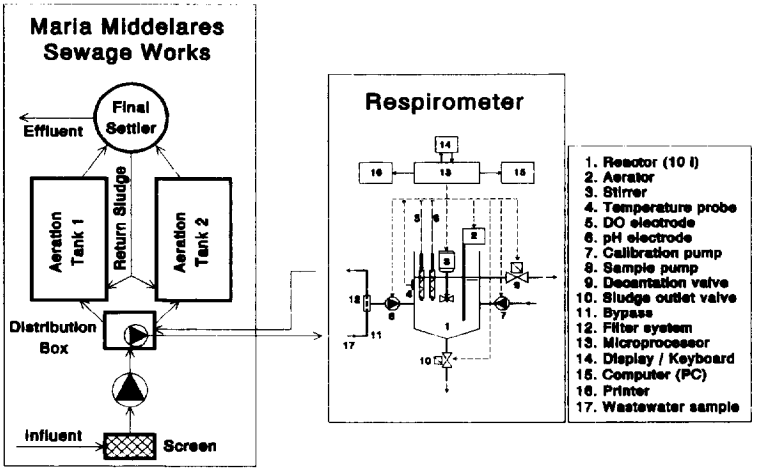

Figure 2. Scheme of the Maria Middelares WWTP and the RODTOX respirometer.

Experimental design

The 6 months experiment was designed in two phases. In a first phase the normal performance of the plant was monitored systematically in terms of COD and NH_4^+-N removal. The reliability of the RODTOX for stBOD measurement was evaluated during these first three months. In the second phase the reliability of the RODTOX for toxicity detection was checked by deliberate intoxication experiments with creoline. The intoxication experiment was performed as follows. First, the toxicity of creoline was measured in the laboratory with the procedure of Kong *et al.* (1993). The IC_{20} value was used to determine the dosage of creoline for the first intoxication experiment. If deterioration of plant performance was not observed, the second intoxication experiment was performed one week later with a fivefold creoline concentration. This intoxication experiment was continued until plant performance had significantly deteriorated.

Parameters monitored during the experimental period

The stBOD, % inhibition and all DO data of the RODTOX were collected with a dedicated data acquisition program (Willems, 1991). Wastewater BOD_5^{20} was quantified with a Sapromat device. COD, Kj- N, NH_4^+-N, NO_2^-+NO_3^--N, SVI and TSS were determined according to Standard Methods (APHA, 1989).

Microtox

The principle of this toxicity test is to measure the change in light output of a luminescent marine bacterium (*Photobacterium phosphoreum*) in presence of toxicants. The 32% toxicity screen procedure was used. The test procedure is described in detail in the Beckman Operating Manual.

RESULTS

Performance of the treatment plant

In order to evaluate the performance of the proposed respirometric method, it is necessary to have good insight into the normal operation of the treatment plant, so that the effect of toxicants can be extracted from the plant performance data. To this end an intense measuring campaign was initiated. First of all, the hydrodynamic properties of the WWTP were evaluated with tracer experiments. Second, the installed respirometer was allowed to assess influent load variations with minimum analytical effort. Finally, daily samples were taken to the lab for analysis of influent and effluent COD, Kj-N and TSS, and ML(V)SS and SVI.

Figure 3 illustrates the particular nature of the treatment plants' flow regime. As the influent pumps are controlled with a level switch, a bang-bang influent flow regime is superimposed on the constant recycle flow rate of 8 m^3/h. The data given in Fig. 3 are the conductivity and flow rates of the mixed liquor leaving the aeration tanks. The pulse-decay flow pattern is caused by the propagation of this hydraulic disturbance through the treatment plant. Evidently, these data would allow detailed modelling of the systems' hydrodynamics (Olsson and Stephenson, 1985). The conductivity profile measured at the outlet of the aeration tank (Fig. 3), was obtained after pulse addition of 20 kg NaCl. The data show good mixing properties in the aeration tank, which will facilitate interpretation of the toxicity experimental data.

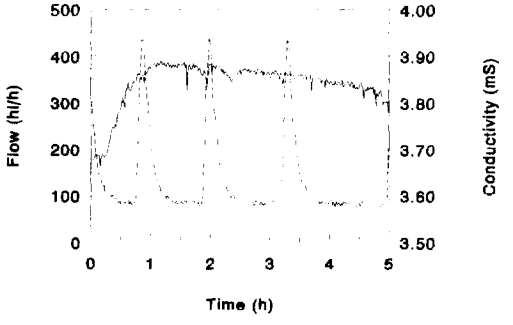

Figure 3. Conductivity (full line) and flow through the aeration tank (dashed line) during the tracer experiment.

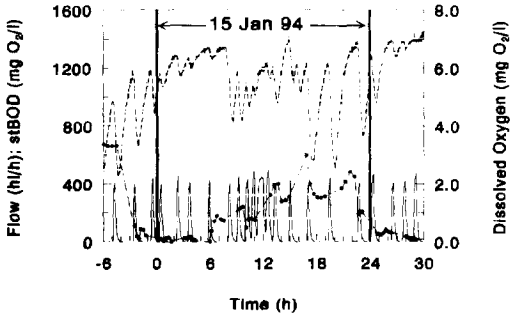

Figure 4. Influent organic load (dots) and flow variations (full line) and corresponding aerator DO (dashed line).

Second, the use of the respirometer for influent short-term BOD allowed us to gain rather detailed insight into its typical daily evolution. Kong *et al.* (1994b) evaluated whether these stBOD data correlate with other

influent parameters. They found that stBOD is a reasonable indicator of both the organic and nitrogen load. A typical daily profile of flow and load is given in Fig. 4. One notices that peak flow is observed in the morning (increased frequency of pump activity) while the pollutant loading peaks in the afternoon. This evolution is of course related to the working hours in the hospital. A nice relation can be observed between the measured influent characteristics and the DO time course in the aeration tanks. The pulse-wise addition of wastewater due to the influent flow control results in rather important DO dynamics that are proportional to the waste concentration. The fast response of the DO probe located near the outlet of the aeration tanks after activation of the influent pump confirms that the tanks are well mixed.

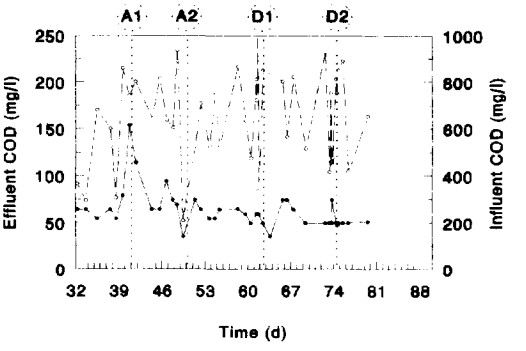

Figure 5. Influent (dashed line) and effluent (full line) COD in February/March. Vertical lines indicate RODTOX alarms.

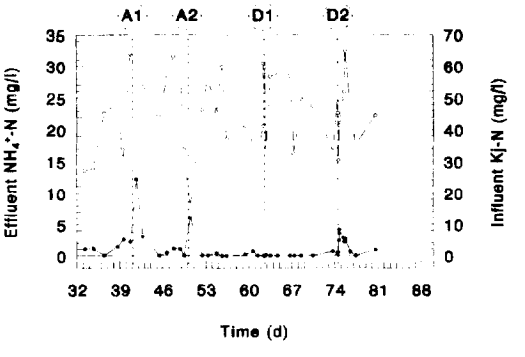

Figure 6. Influent (dashed line) and effluent N (full line) in February/March. Vertical lines indicate RODTOX alarms.

The average annual performance of the plant in 1992–1993 was characterized by a COD removal above 90 percent, while BOD_5^{20} removal was nearly 99 percent. Total nitrogen removal was only 52–67% because no anoxic stage is included in the plant. The COD and NH_4^+-N removal, SVI and TSS of effluent were chosen as monitored performance parameters of the wastewater treatment plant. During the 6-month experimental period, the COD and NH_4^+-N removal efficiency ranged between 82–100% and SVI's were always below 65 ml/g. The effluent quality for February/March 1994 (Figs 5 and 6) shows that total COD and NH_4^+-N are below 100 and 2 mg/l, respectively, except for the toxicity events described below.

Detection of accidental intoxication

In February 1994, the RODTOX activated the toxicity alarm twice. On day 41 (event A1) and 50 (event A2), the % inhibition obtained from the traditional data interpretation method (eqn (2)) surpassed the preset alarm levels of 20 %, triggering the alarm (for details see Kong *et al.*, 1994b). Plant performance effectively decreased on the day after the RODTOX gave the toxic alarm on both occasions (Figs 5 and 6). After event A1, effluent COD and NH_4^+-N concentrations went up to 150 and 12 mg/l, respectively; for event A2, only ammonia increased to 6 mg N/l, i.e. only nitrification was affected. The corresponding influent data show that the increased effluent concentrations were not due to an increased loading.

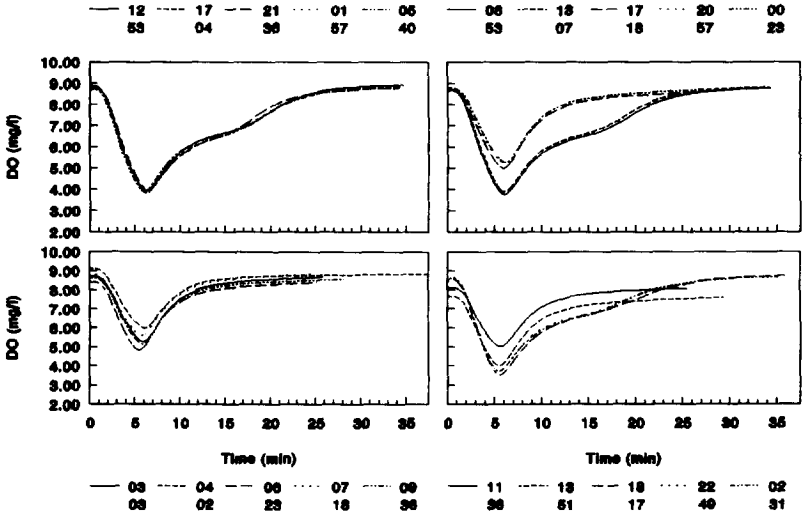

Figure 7. Sequence of respirograms collected during event A2 (February 17–20 1994). The start of each respirogram is indicated in the legend as HH:MM.

Effluent TSS and SVI did not show significant changes. After an inquiry it was found that wastewater originating from the cleaning of the chemical storage basement of the hospital laboratory was the cause of the second toxic spill. Yet, the reason which caused the first sludge intoxication remains unknown.

In the sequel, the results of the model-based data interpretation method are illustrated for event A2. (Similar results were obtained for event A1, data not shown.) In Fig. 7, part of the raw data – a sequence of twenty respirograms – of event A2 are summarized. Respirogram 1 starts on February 17th at 12:53. The first five respirograms give an indication of the excellent stability of the sludge activity and the reproducibility of the respirometer, i.e. the respirograms overlap completely. In the next five respirograms, one clearly observes a sudden change of the shape of the respirogram between respirogram 7 and 8 (between 13:07 and 17:18 on February 18th). In between these calibration injections, the toxic wastewater must have entered the treatment plant. For the next five respirograms no change is noticed. However, in the last sequence, one observes that, first, the baseline decreases and from respirogram 18 onwards, the typical shoulder-shape found before is back. Although this inspection of the raw data reveals the effect of the toxicant on the interaction between the sludge and the calibration mixture of acetate and ammonia, the question remains whether more quantitative information can be retrieved by model identification.

The model of Table 2 was applied to each of the respirograms. Each time both the more complex Double Monod model and the simpler Single Monod model were identified. The estimates of the identifiable biokinetic parameter combinations (eqn (6)) are summarized in Fig. 8 (top 4 graphs). Note that Dataset 1 corresponds with the first respirogram depicted in Fig. 7. Before the outcome of the estimation may be interpreted, it must be decided whether the Single or Double Monod model gives the best description of the

respirograms. This model selection is based on the criteria given in the lower 4 graphs of Fig. 8. The fit performance (expressed as the logarithm of the mean square error $J/(n-p)$, with n the number of data and p the number of estimated parameters) clearly points to a change in behaviour between respirogram 7 and 8. More specifically, the process changes from Double Monod to Single Monod type biodegradation. In other words, one of the substrates added is no longer oxidized.

As will become evident from the parameter interpretation, nitrification is inhibited completely by the toxicant. Still, it appears that the system is capable to return to its initial behaviour after Dataset 17.

Similar conclusions are drawn from the AIC-criterion which penalizes more complex models ($AIC = n.log[J/n]+2p$). To facilitate the evaluation, the effects of different dataset sizes on the AIC-criterion (e.g. Dataset 12 in Fig. 8) were eliminated by calculating the ratio of AIC-values obtained for the two models (Fig. 8). If the AIC-ratio is nearly one (e.g. below 1.5), one can decide that both models give nearly identical descriptions of process behaviour. Hence, one will then select the simpler model.

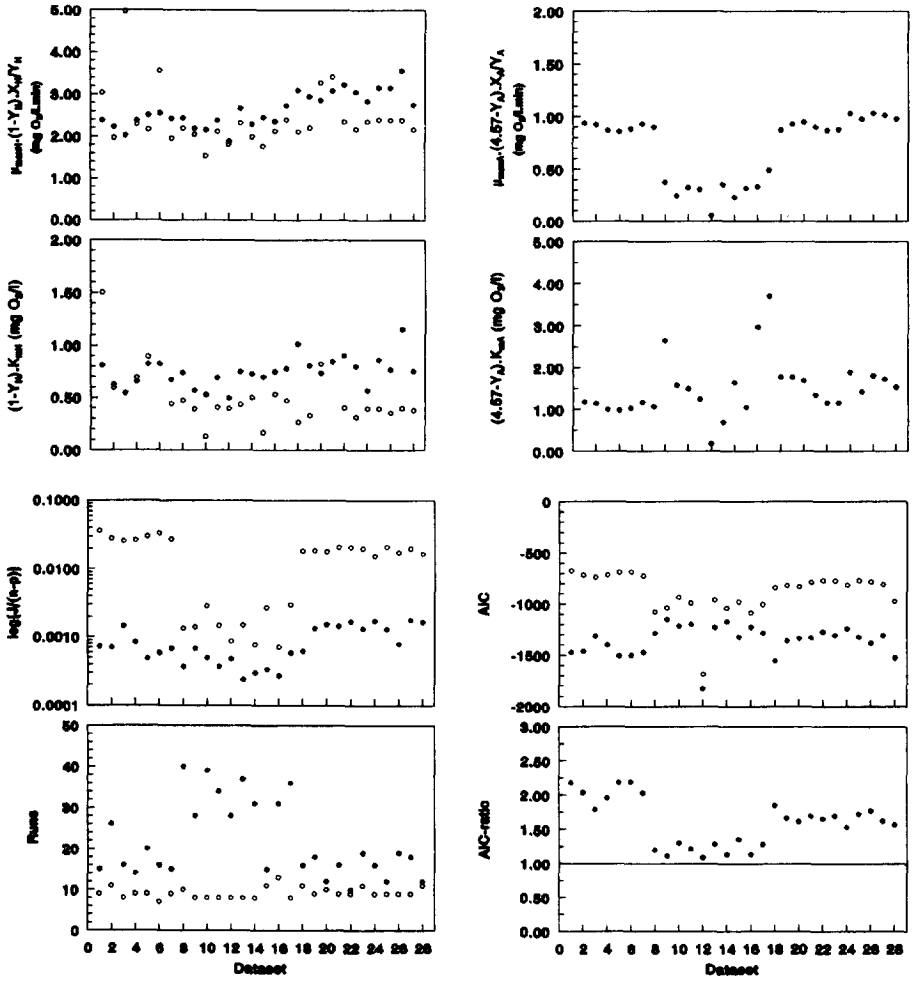

Figure 8. Double Monod (filled symbols) and Single Monod model (open symbols) identification for event A2. Biokinetic parameter combinations for heterotrophic (top left 2) and autotrophic populations (top right 2) and model selection criteria (lower 4 graphs).

A last selection criterion used is based on the number of runs, i.e. the number of sign changes found in the residual sequence. The higher this number the better the correspondence between model and data can be considered. It was advocated before as a good technique for model selection (Vanrolleghem *et al.*, 1994b). Here, however, it would lead to the opposite conclusion than for the other criteria: Especially in the period where the Single Monod model would be preferred, this method points to the Double Monod model. This can be explained by the fact that some unmodelled dynamics remain in the residual sequences. As the more complex model has more degrees of freedom – especially when process behaviour becomes less complex – it can accommodate for part of these dynamics. This will automatically lead to an increase in the number of runs. Hence, this 'runs' method can be applied only if process description is nearly perfect.

The estimates of the biokinetic parameters of the heterotrophic and autotrophic populations are compiled in Fig. 8. Before interpreting these figures, the reader is referred to the paper by Vanrolleghem and Keesman (1996) where the relative parameter estimation error was found to be approximately 5 to 20 percent depending on the parameter considered, i.e. for the parameter combination involving maximum growth rates a better precision is obtained than for the combination with the affinity constant.

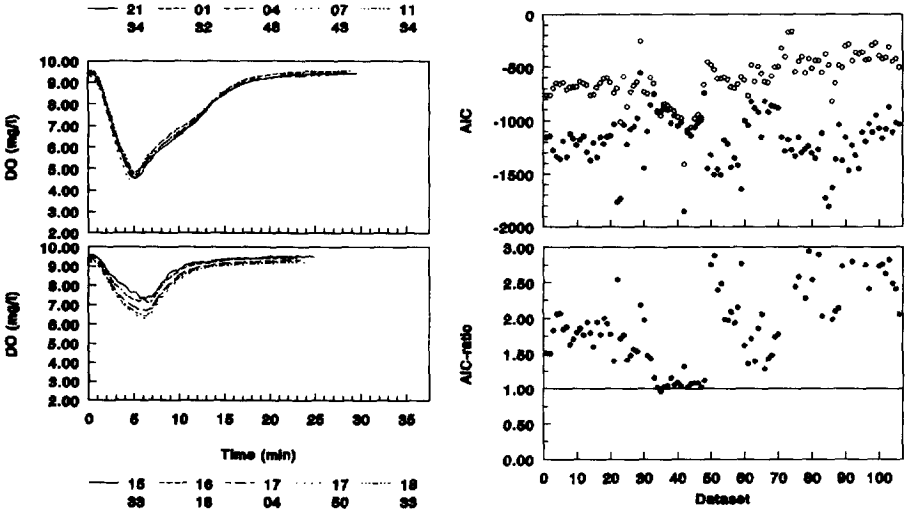

Figure 9. Selected respirograms (left) of event D2. Start of respirograms is indicated in the legends as HH:MM. Upper respirograms are taken from March 13–14, lower from March 15. AIC-based model selection (right) for the period March 11–21 (Double Monod model: filled symbols, Single Monod model: open symbols).

It is important to keep in mind that a switch to the Single Monod model occurs between Dataset 8 and 17. Hence, one must switch attention from filled to open symbols for these Datasets.

The parameter combination involving μ_{maxH} is not significantly affected by the presence of the toxicant. For Y_H=0.67 and X_H=1 g COD/l, μ_{maxH} amounts to 6.5 d^{-1} (at 20°C). The K_{mH} related parameter combination on the other hand appears affected although caution should be taken with this interpretation as this parameter is known to be the most difficult to estimate from this type of experiments (Dochain *et al.*, 1995). With the assumed yield factor, a Monod constant of approx. 2.25 mg acetate COD/l is obtained.

For the autotrophic population, rather constant growth rates and ammonia Monod constants are obtained during non-inhibitory conditions. With Y_A set to 0.24 g COD/g N and X_A=0.25 g COD/l, one obtains μ_{maxA}=0.32 d^{-1} and K_{mA}=0.28 mg N/l. An important remark relates to the autotrophic parameter values of the Double Monod model obtained in the period where the Single Monod model is to be preferred. Here the

additional degrees of freedom of the Double Monod model are used to fit unmodelled dynamics that have nothing to do with nitrification. Hence, a non-sense scatter of parameter values is observed.

Detection of deliberate intoxication

In order to further confirm the reliability of this respirometric principle for toxicity detection, a full-scale plant intoxication was simulated. Creoline disinfectant was used as a model toxicant. Prior to the experiment, IC_{20} and IC_{50} of creoline were assessed for the hospital sludge to estimate the expected intoxication dose. The IC_{20} and IC_{50} were 7.5 and 40 ppm of creoline respectively (Kong *et al.*, 1994b).

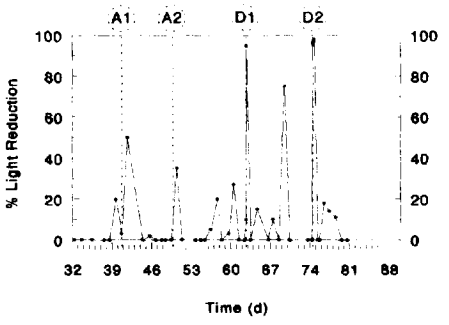

Figure 10. Microtox toxicity results for February/March. Vertical lines indicate RODTOX alarms.

The intoxication was simulated by a deliberate discharge of toxic wastewater containing 380 ppm of creoline. On March 3, this toxic wastewater entered the plant. After around 50 minutes, the RODTOX detected the toxic input and gave toxic alarm (Event D1). The toxic wastewater addition was interrupted when the creoline concentration in the aeration tank had become 5 ppm. It was found that the effluent quality, as indicated by the COD and NH_4^+-N, was not affected (Figs 5 and 6). This indicated that the toxicity detection was in due time to take remedial actions such as given in Table 1.

Eleven days later, on March 15, a second intoxication experiment was conducted with a similar wastewater (event D2). Again, after the toxic water started to enter (March 15, 9:24) the RODTOX gave toxicity alarm. However, this time the toxic wastewater supply was not interrupted. Only when the creoline concentration in the aeration tank reached 25 ppm, addition was stopped. Figure 6 shows that the effluent NH_4^+-N concentration increased within a few hours from below 1 ppm to 4.5 ppm at 16:45, indicating significant deterioration of effluent quality (Fig. 6).

In Figure 9 respirograms are given of the period before creoline was added (upper left, Datasets 16–20) and after addition had started (lower left, Datasets 36–40). Again, one observes the loss of nitrifying activity. This is confirmed by the AIC model selection criteria that detect a model structure change at Dataset 33 (March 15, 12:38) and a return to the Double Monod process model with Dataset 50 (March 16, 03:45). The advantage of using AIC-ratios instead of the raw AIC-results is illustrated by the two right plots in Fig. 9. Compared to the results of event A2 (Fig. 8), however, the AIC-ratios are closer to unity for the period where both nitrifiers and heterotrophs are active. Hence, the power of the experiments to discriminate between Single and Double Monod models is lower than for event A2. This is caused by the changed sludge characteristics, as can be seen from a comparison of 'Double Monod'-type respirograms of periods A2 and D2. Still, it is possible to obtain more reliable model selection if the calibration mixture is adjusted. Optimal design techniques for this can be found in Vanrolleghem and Van Daele (1994).

Comparison with Microtox lab toxicity test

During the experimental period the toxicity of the influent samples was also evaluated with the Microtox test. The inhibition percentages of the light emission for February and March 1994 are presented in Fig. 10. On February 9 (A1) and 18 (A2), the light output by the test culture was reduced by 50 and 36 %. On March 3 (D1) and 15 (D2), the light reduction approached 100%. These intoxications correspond with the toxicity alarms given by the on-line respirometric procedure. On March 9 the Microtox gave a false alarm as it detected 75% light output reduction, but this was due to a red coloured influent.

CONCLUSIONS

It is shown that model-based interpretation of DO data collected from In-Sensor-Experiments in a respirometer installed at the influent line of a wastewater treatment plant allows on-line toxicity detection. The procedure was evaluated at a full-scale sewage works. Both accidental and deliberate intoxication events were detected. Experimental evidence showed that detection is in due time to protect the plant.

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