River Water Quality Model no. 1 (RWQM1): Case study II. Oxygen and nitrogen conversion processes in the River Glatt (Switzerland)

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Abstract Various simplifications of the river water quality model no. 1 are applied to data sets from the river Glatt in Switzerland. In a first application, the biomass responsible for nitrogen and oxygen conversion processes is quantified based on known reaeration rates, measured concentrations of ammonia, nitrite and oxygen and assumed growth parameters of algae and bacteria. In a second application, the model is extended to calculate chemical equilibria of inorganic carbon compounds dissolved in the water and daily variations in pH. The influence of partially unknown inflow concentrations and of calcite precipitation on fluctuations in electrical conductivity and pH are discussed. In the last model, the processes of growth of sessile algae and bacteria, detachment of algae, and grazing by benthic organisms are introduced. Due to lack of data for quantifying these processes, this last model application is speculative. Nevertheless, it is interesting because it shows a direction to which river water quality modelling would have to proceed in order to increase its predictive capabilities.

Keywords Ammonia; dissolved oxygen; nitrite; nitrification; pH; calcite precipitation; primary production; respiration; rivers; water quality models

Introduction
In a series of three papers, the River Water Quality Model no. 1 was presented as a scientific and technical base for formulating river water quality models (Shanahan et al., 2001; Reichert et al., 2001b, Vanrolleghem et al., 2001). It is the goal of the present case study to demonstrate the application of various simplified versions of this model to the river Glatt in Switzerland. In contrast to previous modelling studies for this river, which were primarily devoted to identification of processes (Reichert et al., 2001a; Uehlinger et al. 2001), hypothetic applications of advanced model features are discussed in the present paper. Such applications can show the direction to which river water quality modelling would have to proceed in order to improve its predictive capabilities. In addition such applications can give impetus for more experimental work to be done for testing emerging new hypotheses.

Study site
The river Glatt is a small river of about 35 km length flowing from lake Greifensee to the Rhine river. Its characteristics change from an unpolluted lake outlet to a slowly flowing, heavily polluted river with a small slope north of Zürich, and finally, to a relatively steep, highly aerated river with small drops every 50 m and some cascades. This study, as well as the previous studies mentioned above, focus on the last part of the river of about 10 km length. This river reach can best be used for the investigation of conversion processes of substances transported with the river water, because there are no significant dry weather tributaries. For this river reach, upstream and downstream on-line measurements of temperature, pH, ammonia, nitrite and oxygen concentrations are available from six measurement campaigns with duration between a few days and a few weeks (Berg, 1991, Kändler, unpublished). In addition, on-line measurements of temperature, pH and oxygen
concentration, and cumulative samples of many other substances are available at the down-
stream site from the Swiss National River Survey Program (NADUF).

Review of previous modelling studies
Because it has been shown experimentally that conversion processes in samples from the
water column are much slower than those observed in the river, all modelling approaches
concentrate on conversion of substances dissolved in the water column caused by sessile
bacteria and algae attached to the river bed.

The goals of the first study (Reichert et al., 2001a) were to determine nitrification, pro-
duction and respiration rates in the river and to find correlation between environmental fac-
tors and oxygen and nitrogen conversion rates. Stoichiometric coefficients of the simple
model applied in this study were determined with the aid of a mass composition for organic
substances that considered only the elements C, H, O and N. For the dissolved substances
ammonia ($S_{NH4}$), nitrite ($S NO2$), and oxygen ($S O2$), conversion rates were formulated with a
linear dependence of algae growth on light intensity, a constant community respiration rate,
and with Monod-type limitation factors for oxygen and ammonia or nitrite for 1st and 2nd
stage nitrification, respectively. The parameters of these transformation rates were estimat-
ed using upstream and downstream on-line measurements for ammonia, nitrite and oxygen
of all six measurement campaigns mentioned above (Berg, 1991, Kändler, unpublished; the
gas exchange coefficient for oxygen was determined independently with SF6 volatilisation
experiments). The most important results of the study were the following.

- For each of the six measurement campaigns a good fit was possible after adjusting the
six model parameters. However, the values of the parameters differed from one
measurement campaign to the other.
- No significant correlation between environmental parameters and conversion rate
parameters was found.

This led to the following conclusions.
- The model is of an adequate complexity for the description of short term dynamics of
ammonia, nitrite and oxygen concentrations (daily variations within periods of a few
days).
- Over the time scale of a few days to a few weeks, nitrogen and oxygen conversion rate
parameters do not change significantly. Since these rates are caused by sessile algae and
bacteria, this implies the presence of a limiting factor for the accumulation of active
algae and bacteria such as detachment, grazing, or a limiting effect of active biomass in
biofilms due to diffusion or shading.
- Due to the absence of a mechanistic description of the limiting factor for the accumula-
tion of active biomass, the model cannot be used for long-term prediction or for the pre-
diction of oxygen and nitrogen dynamics under changed external driving conditions
(e.g. improved wastewater treatment).

The most important problem of the investigation described above was the inability to
find a significant correlation between conversion rate parameters and environmental fac-
tors. One reason for this result was the small number of measurement campaigns that could
not be increased significantly.

In order to obtain a better statistical foundation at least for production and respiration
rate parameters, the model was simplified to a model only for dissolved oxygen. This model
could be calibrated with the downstream on-line measurements of oxygen alone (Uehlinger
et al., 2000). These are available over many years from the Swiss National River Survey
Program (NADUF). With this model, 123 dry weather periods of 3 days length within a
period of 6 years could be evaluated. One respiration parameter (total community
respiration including nitrification) and two production parameters were fitted for all 123
investigation periods and a correlation analysis with discharge, time, temperature, seasonal temperature gradient, time since last flood, and global radiation was performed. This evaluation led to the following results:

- The environmental parameters with most significant influence were temperature, seasonal temperature gradient, time, and global radiation (used for production parameters only).
- There was no significant effect of discharge or time since last flood.

The conclusions were, that in contrast to gravel-bed rivers (Uehlinger et al., 1996), floods have no significant effect on production and respiration in the river Glatt with its more stable river bed and that production and respiration activity is dominated by the seasonal effect.

Goals of the present study

The focus of the previous studies summarised above was to quantify nitrogen and oxygen conversion rates. This was done with parsimonious models that use coefficients in empirically formulated conversion rates as model parameters. These models do not describe changes in algal and bacterial densities mechanistically. Therefore, they are not able to predict conversion rates under changed external driving conditions (e.g. improved wastewater treatment). The goal of the present study is to perform speculative applications of adequate submodels of the river water quality model no. 1 in order to demonstrate how an increase in the predictive capability of river water quality models could be achieved. This goal is approached by discussing three submodels of increasing complexity. The three submodels of the river water quality model no. 1 applied in these three steps as well as the results of their application to the river Glatt are described in the following three sections.

All results shown in the following sections were gained by integrating the partial differential equations for river hydraulics, substance transport and substance conversion with the simulation and parameter identification program AQUASIM (Reichert 1994; 1995; http://www.aquasim.eawag.ch).

Submodel for oxygen, nitrogen, and phosphorus conversion by constant benthic biomass

The first submodel of the River Water Quality Model no. 1 is described qualitatively in Table 1. In addition to the processes shown in this matrix, gas exchange of dissolved oxygen at the cascades and along the river is considered. Bacterial densities are assumed to be constant and are used as model parameters.

The submodel shown in Table 1 is similar to the model used in the first case study mentioned above (Reichert et al., 2001). The major difference to this model is that here the values of growth parameters and yields of algae and bacteria are assumed and that surface densities of sessile algae and bacteria are used as model parameters instead of more direct conversion rate parameters for nitrification, production and respiration. This leads to more speculative results but it is a good first step towards a model with better predictive capabilities that tries to simulate the dynamics of algae and bacteria. A difference of minor importance is the consideration of nitrate, $S_{NO3}$, dissolved organic substrate, $S_S$, and phosphate, $S_{HPO4}$, as additional state variables.

Table 2 summarises the input data used for the simulations with the model shown in Table 1. In addition to these data, light intensity and atmospheric pressure were used from a nearby measurement site of the Swiss Meteorological Institute and water temperature from Berg (1991).

All parameter values of the model were taken from the numerical example given in Reichert et al. (2001b) with the exception of $K_I$, the value of which was increased to 2000 W/m² in order to account for the use of light intensity at the water surface instead of...
light intensity at the river bed (there was no significant light limitation or inhibition observed). The bacterial densities that are model parameters and not state variables in this simplified model were used to adapt the model results to the measurements. Table 3 gives the values of the model parameters for two measurement campaigns in July and November 1990 and Figure 1 shows measured and calculated upstream and downstream concentrations of oxygen, ammonia and nitrate.

As already stated in Reichert et al. (2001a) the good agreement of calculated with measured concentrations for this simple model indicates that there is no significant change of active biomass in the river during the measurement periods.

**Table 1** First submodel of the river water quality model no. 1 as it is used for the present investigation. Anoxic processes, processes and state variables for dissolved inorganic carbon compounds and all particulate state variables are omitted. Instead, algal and bacterial surface densities are used as model parameters

<table>
<thead>
<tr>
<th>Component → i</th>
<th>j</th>
<th>Process ↓</th>
<th>( i )</th>
<th>( s_5 )</th>
<th>( s_{NH4} )</th>
<th>( s_{NO2} )</th>
<th>( s_{NO3} )</th>
<th>( s_{NPO4} )</th>
<th>( s_{O2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1a) Aerobic degradation of heterotrophs with NH4</td>
<td>1</td>
<td>( + )</td>
<td>( - )</td>
<td>( ? )</td>
<td>( ? )</td>
<td>( - )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(1b) Aerobic growth of heterotrophs with NO3</td>
<td>1</td>
<td>( - )</td>
<td>( ? )</td>
<td>( ? )</td>
<td>( - )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(2) Aerobic respiration of heterotrophs</td>
<td>2</td>
<td>( + )</td>
<td>( + )</td>
<td>( - )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(5) Growth of 1st-stage nitrifiers</td>
<td>5</td>
<td>( - )</td>
<td>( + )</td>
<td>( - )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(6) Aerobic respiration of 1st-stage nitrifiers</td>
<td>6</td>
<td>( + )</td>
<td>( + )</td>
<td>( - )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(7) Growth of 2nd-stage nitrifiers</td>
<td>7</td>
<td>( - )</td>
<td>( + )</td>
<td>( - )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(8) Aerobic respiration of 2nd-stage nitrifiers</td>
<td>8</td>
<td>( + )</td>
<td>( + )</td>
<td>( - )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(9a) Growth of algae with NH4</td>
<td>9</td>
<td>( - )</td>
<td>( - )</td>
<td>( + )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(9b) Growth of algae with NO3</td>
<td>9</td>
<td>( - )</td>
<td>( - )</td>
<td>( + )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(10) Aerobic respiration of algae</td>
<td>10</td>
<td>( + )</td>
<td>( + )</td>
<td>( - )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(11) Death of algae</td>
<td>11</td>
<td>( + )</td>
<td>( + )</td>
<td>( + )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(15) Hydrolysis</td>
<td>15</td>
<td>( + )</td>
<td>( + )</td>
<td>( + )</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

**Table 2** Input concentrations used for the model described in Table 1

<table>
<thead>
<tr>
<th>Variable</th>
<th>July 90</th>
<th>Nov. 90</th>
<th>Unit</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>( S_5 )</td>
<td>7.7</td>
<td>6.6</td>
<td>gCOD/m³</td>
<td>based on cumulative sample of river survey program</td>
</tr>
<tr>
<td>( S_{NH4} )</td>
<td>measured time series of NH₃+NH₄</td>
<td>gN/m³</td>
<td>see Figure 1</td>
<td></td>
</tr>
<tr>
<td>( S_{NO2} )</td>
<td>measured time series</td>
<td>gN/m³</td>
<td>see Figure 1</td>
<td></td>
</tr>
<tr>
<td>( S_{NO3} )</td>
<td>4.5</td>
<td>4.5</td>
<td>gN/m³</td>
<td>based on cumulative sample of river survey program</td>
</tr>
<tr>
<td>( S_{NPO4} )</td>
<td>0.28</td>
<td>0.21</td>
<td>gP/m³</td>
<td>based on cumulative sample of river survey program</td>
</tr>
<tr>
<td>( S_{O2} )</td>
<td>measured time series.</td>
<td>gO/m³</td>
<td>see Figure 1</td>
<td></td>
</tr>
</tbody>
</table>

**Table 3** Parameter values adjusted for adapting the simulated results to the downstream measurements. The width of the river is about 17 m (biomass surface densities can be obtained by a division by 17 m)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>July 1990</th>
<th>Nov. 1990</th>
<th>Unit</th>
<th>Parameter</th>
<th>July 1990</th>
<th>Nov. 1990</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>( X_{Algs} )</td>
<td>650</td>
<td>800</td>
<td>gCOD/m³</td>
<td>( X_{N1s} )</td>
<td>20</td>
<td>50</td>
<td>gCOD/m³</td>
</tr>
<tr>
<td>( X_{Hs} )</td>
<td>350</td>
<td>0</td>
<td>gCOD/m³</td>
<td>( X_{N2s} )</td>
<td>3.5</td>
<td>15</td>
<td>gCOD/m³</td>
</tr>
<tr>
<td>( X_{Ss} )</td>
<td>250</td>
<td>0</td>
<td>gCOD/m³</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Extension of the submodel to the calculation of dissolved carbonate equilibria, calcite precipitation and pH

Although the first submodel shown in Table 1 could describe the behaviour of the most important dissolved compounds in the river, it is interesting to extend the dissolved variables in the model to the calculation of the pH value. This would make it possible to calculate the concentration of NH$_3$ (toxic for fish) and to use pH dependent rate expressions (of special importance for nitrification, see Quinlan (1984) and Boon and Laudenout 1962). The second submodel of the river water quality model no. 1 shown in Table 4 extends the submodel shown in Table 1 by the state variables and processes required for this task. Gas exchange of carbon dioxide is taken into account in addition to gas exchange of oxygen. In addition, constant values, $S_K$, $S_{Mg}$, $S_{Na}$, $S_C$, and $S_{SO4}$ for the concentration of potassium, magnesium, sodium, chlorine and sulfate were assumed in order to make a calculation of electrical conductivity possible. Note that only the most essential variables for the calculation of pH were introduced. More complete pH models can be found in Chapman (1982), Yeh and Tripathi (1991) and Runkel et al. (1996a and b).

Because pH dependence of process rates is neglected in the model, this second submodel leads to the same results for nutrients and oxygen as the first submodel (see Figure 1). However, dissolved inorganic carbon compounds, protons (and pH), hydroxyl ions and calcium ions can be calculated additionally. This leads also to an increased number of inflow concentrations to be provided at the upstream end of the river section. Table 5 gives an overview on the origin of the data used for the input. Because there were no quasi-continuous measurements available for some of the modelled substances, the concentrations of some substances were assumed to be constant at a value measured in cumulative samples of the

![Graphs showing measured and calculated concentrations of oxygen, ammonia, and nitrite for July and November 1990](https://iwaponline.com/wst/article-pdf/43/5/51/429589/51.pdf)
Table 4 Second submodel of the river water quality model no. 1 as it is used for the present investigation. The model is extended by the inorganic carbon compounds and the calcium ion used for pH calculation and by the corresponding chemical equilibrium processes.

Table 5 Input concentrations used for the model described in Table 5. In addition $S_K$ (4.2, 3.9 gK/m$^3$), $S_{Mg}$ (16, 16 gMg/m$^3$), $S_{Na}$ (17, 16 gNa/m$^3$), $S_{Cl}$ (23, 24 gCl/m$^3$), and $S_{SO4}$ (22, 23 gSO4/m$^3$), are introduced as constant substance concentrations in order to consider the most important ions for electrical conductivity (values are given for the two simulation runs for July and November 1990).
river survey program. The inflow concentration of bicarbonate ions was then calculated from a charge balance according to

\[
S_{\text{HCO}_3} = \frac{12}{1 + 2K_{eq,2} / S_{\text{H}}} \left\{ S_{\text{H}} - S_{\text{OH}} + \frac{S_{\text{NH}_4}}{14} - \frac{S_{\text{NO}_2}}{14} - \frac{S_{\text{NO}_3}}{14} - \frac{S_{\text{HPO}_4}}{31} \right. \\
\left. + \frac{S_{\text{HPO}_4}}{31} \left[ \frac{2S_{\text{SO}_4}}{96} + \frac{2S_{\text{Ca}}}{40} + \frac{2S_{\text{Mg}}}{24.3} + \frac{S_{\text{K}}}{39} + \frac{S_{\text{Na}}}{23} \right] \right\} \tag{1}
\]

Figure 2 shows the results for some of the additional state variables and derived variables for the second submodel. For these simulations, the gas exchange efficiency for CO₂ at the cascades and the kinetic coefficient for calcium dissolution/precipitation had been adjusted. Calculated values of pH (Figure 2, top left) are qualitatively correct, however, there is a time shift in comparison to the measurements. Electrical conductivity is in the correct order of magnitude (Figure 2, top right). The differences in the daily variations is probably due to (unknown) variations in some ion concentrations at the upstream end of the river reach (for the calculation, due to lack of data, most upstream ion concentrations were set to constant values, see Table 5). The plots for calcium and CO₂ in Figure 2 show that the river is significantly supersaturated with both components. The dashed lines show the equilibrium levels for calcium based on the current CO₃ concentration and for CO₂ the equilibrium with the atmosphere. Assumption of equilibration of calcium with calcite through precipitation (by increasing the value of \( k_{eq,0} \)) would significantly diminish the amplitude of pH variations.

Hypothetical simulation of the dynamics of benthic biomass

The third submodel of the River Water Quality Model no. 1 used for a more speculative simulation is shown in Table 5. In addition to the dissolved state variables of the first model
shown in Table 1, it contains particulate state variables for sessile algae and bacteria (\(X_{H,s}, X_{N1,s}, X_{N2,s}, X_{ALG,s}\)), for benthic consumers (\(X_{CON,s}\)), for sedimented organic material (\(X_{S,s}, X_{I,s}\)) and for suspended organic material (\(X_S, X_I\)).

Modelling of sessile or benthic organisms requires some additional considerations. In order to make it easy to fulfil mass balances even in the case of fluctuating water levels, it is advantageous to introduce sessile or benthic biomass per unit river length instead of per unit river bed surface. In Table 6 such masses per unit length are indicated with an index “s” (e.g. \(X_{H,s}\) denotes the mass of heterotrophic bacteria per unit river length). The coefficients in the stoichiometric matrix that convert from substances dissolved or suspended in the water column to substances attached to the river bed must then be multiplied with the wetted cross-sectional area \(A\) of the river (this is the water volume per unit river length).

As an additional physical process, detachment of attached biomass to the water column and sedimentation of suspended organic material must be taken into account. The process rates in Reichert et al. (2001b) are formulated with in-situ nutrient and oxygen concentrations and with in-situ light conditions. If the benthic biofilm in the river is modelled on the basis of surface densities or masses per unit river length only, limiting effects due to self-shading and diffusion of nutrients into the biofilm are not considered. An empirical consideration of this effect is possible with a limiting factor for growth of algae and bacteria with increasing algal or bacterial biomass. This can be implemented by a factor

\[
1 + \left(\frac{k_{gro}}{r_{max}}\right)X
\]

in the growth rate of algae and bacteria. A similar factor was also introduced for consumers.

A final extension of the model concerns the assumption of a homogeneous mixture of the
food of the consumers. This may not be realistic for sessile algae and bacteria. Because in contrast to algae, bacteria can grow without light, they can grow on places that may be difficult to access by consumers. This can be considered by multiplying all bacterial concentrations in the rate expression for consumer growth by an empirical factor $\alpha_{BAC}$.

All these additional processes introduce a number of additional model parameters that cannot be identified. Figure 3 shows a simulation of the benthic population based on average nutrient concentration in the water and on actual light, discharge and temperature data in the River Glatt. This figure demonstrates, that simulations can lead to reasonable results (the typical seasonal change of the respiration rate shown in Uehlinger et al., 2001 is roughly reproduced). However, much more data on the algal and bacterial population at the river bed would be necessary in order to identify the parameters of such a river model.

Summary and conclusions

This case study demonstrated the applicability of the River Water Quality Model no. 1 in three steps.

• The application of the first (simplest) submodel demonstrated the capability of reproducing previous results obtained with even simpler models.

• The second application showed the usefulness of the inorganic carbon submodel for modelling pH. With the consideration of pH-dependent rates this could lead to an interesting model extension.

• Finally, the third speculative application demonstrated that the model has the potential to be used for predicting algal and bacterial densities and nutrient and oxygen conversion rates also for changed external driving conditions. However, such a prediction needs much more experience with model parameters and formulations that must be gained by data evaluations for a wide spectrum of river types.

As shown with this case study, prediction of nutrient and oxygen conversion rates in rivers is a difficult task which requires a lot of experience with model formulations and model parameters for a given type of river. We hope the River Water Quality Model no. 1 can help facilitate the exchange of experience among river water quality modellers and thereby can accelerate improvements in predictive power of river water quality models.

Acknowledgements

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