Influence of NOM Concentration on Parameter Sensitivity of a Mechanistic Ozone Decomposition Model

W. T. M. Audenaert*,**, M. Vandevelde**, S. W. H. Van Hulle*,** and I. Nopens*

*BIOMATH, Department of Applied Mathematics, Biometrics and Process Control, Ghent University, Coupure Links 653, 9000 Gent

**EnBiChem Research Group, Department of Industrial Engineering and Technology, University College West Flanders, Graaf Karel de Goedelaan 5, 8500 Kortrijk

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Introduction

Aqueous ozone decomposition proceeds through a complex chain mechanism of radical reactions. A general accepted mechanistic model for ozone decomposition in ultrapure water at acidic to neutral pH is the Staehelin-Bühler-Hoigné (SBH) model (Buhler et al., 1984; Staehelin et al., 1984). When natural organic matter (NOM) is present, the system becomes much more complex and often (semi-)empirical modelling approaches are used to describe ozonation of water and wastewater systems. Mechanistic models, however, can be of great value to gain knowledge in the chemical pathways in view of engineering applications. However, the numerous model parameters and model complexity often restrict their applicability. Model simplification is then an option to cure these drawbacks. A useful tool to determine the most important elementary reactions from a complex kinetic model is sensitivity analysis (Saltelli et al., 2005). In this study, a local sensitivity analysis (SA) is used to distinguish different phases occurring during ozonation in the presence of NOM at different concentrations. A global SA is performed to determine the key parameters.

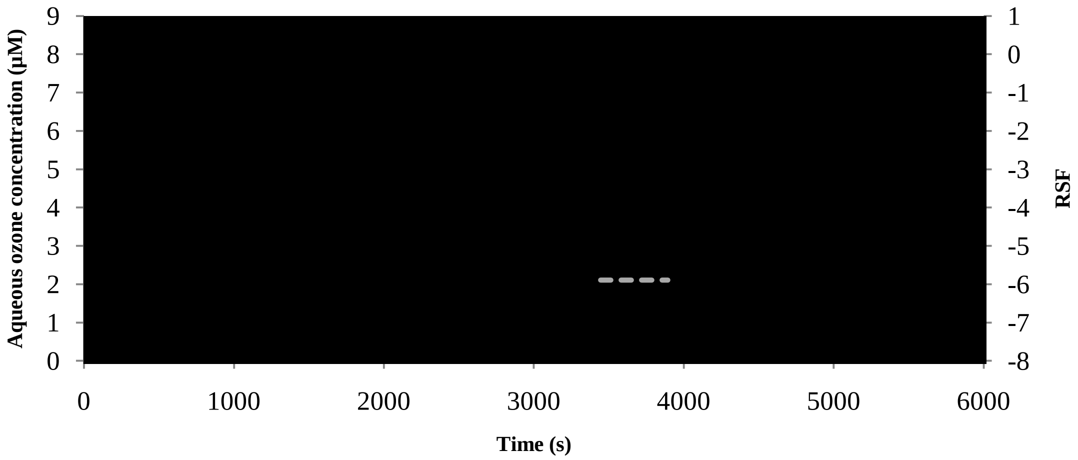
Methods

A semi-batch reactor continuously fed with gaseous ozone was simulated using the SBH model extended with a second order equation describing the reaction between hydroxyl radicals and NOM (Westerhoff et al., 1997). The model assumed that only hydroxyl radicals (not ozone) decomposed NOM with a molar ratio of 1:1. Initial NOM concentrations were varied between 0 and 12 mg L^{-1}. Both simulations and sensitivity analysis were performed using the simulation platform WEST® (Vanhooren et al., 2003) distributed by DHI (mikebydhi.com). A perturbation factor of 0.05 was used in local SAs.

Results

A local SA revealed that only six of the twenty eight kinetic rate constants affected the ozone and hydroxyl radical concentrations over the whole range of tested NOM concentrations. For all influential rate constants, the influence with respect to the ozone concentration significantly decreased with increasing NOM concentrations. The rate constants describing the chain initiation (k_1 and k_2), the rate constant with respect to protonation of the hydroperoxyl anion to form hydrogen peroxide (k_3) and the rate constant for the reaction between ozone and hydroxyl radicals (k_8) were of major importance. The kinetic constant representing scavenging by NOM (k_{31}) also highly affected the hydroxyl radical concentration, even at high NOM levels.

At low NOM concentrations, the ozone concentration showed a dynamic behaviour which can be clearly derived from the central relative sensitivity (CRS) function as shown in Figure 1. During a first phase, sufficient NOM was present to scavenge all hydroxyl radicals which allowed the aqueous ozone concentration to increase. The rate constant describing scavenging by NOM (k_{31}) positively influenced the ozone concentration (the grey dashed line (CRS=0) was added for clarification). When NOM becomes limiting, however, more hydroxyl radicals are available for direct ozone decomposition. In this second phase, the rate constant became negatively influential as rising this parameter implied NOM to be depleted faster and hence, less radicals can be scavenged leading to lower ozone concentrations. At the moment all NOM was depleted, the sensitivity function reached its maximum value. In a third phase, the



ozone concentration significantly decreased and the sensitivity function reached zero.

Figure 1 Sensitivity function of k_{31} with respect to the aqueous ozone concentration; $[NOM]_0$=0.1µM

Results of a global SA are shown in Figure 2. Based on the t-statistic values of the standardized regression coefficients (SRCs), it becomes clear that the influence of the ozone mass transfer coefficient (k_La) and ozone saturation concentration ($[O_3*]$) on the aqueous ozone concentration is very significant (t>1.96). The rate constants that were classified as influential during the local SA also show their impact here.

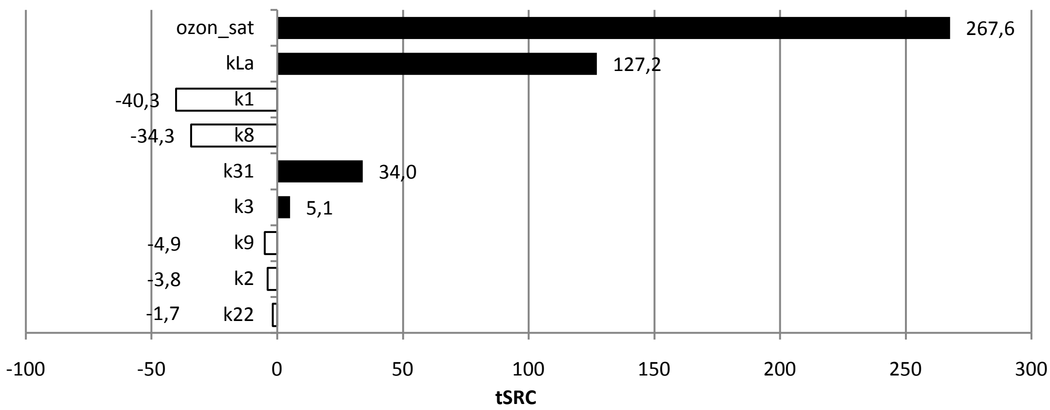


Figure 2 t-statistic values of SRCs from a global SA on ozone concentration (Tornado plot). Parameters sorted from most to least influential (a value above 1.96 means a significant influence)

Conclusions

This study showed that only a few parameters of the SBH model affect the ozone concentration and hence, model simplification should be considered. Furthermore, k_La, $[O_3*]$ and parameters involving NOM seemed to have a large impact on the simulation results. As such it is vital to accurately assess the gas transfer parameters and the NOM content when simulating ozone degradation.

References

Buhler, R.E., Staehelin, J. and Hoigne, J. (1984) Ozone decomposition in water studied by pulse-radiolysis. 1. HO2/O2-and HO3/O3- as intermediates. *J. Phys. Chem*. **88**, 2560-2564.

Staehelin, J., Buhler, R.E. and Hoigne, J. (1984) Ozone decomposition in water studied by pulse-radiolysis. 2. OH and HO4 as chain intermediates. *J. Phys. Chem*. **88**, 5999-6004.

Saltelli, A., Ratto, M., Tarantola, S. and Campolongo, F. (2005) Sensitivity analysis for chemical models. *Chemical Reviews* **105**, 2811-2827.

Vanhooren, H., De Pauw, D., and Vanrolleghem, P.A. (2003) Induction of denitrification in a pilot-scale trickling filter by adding nitrate at high loading rate. *Water Science and Technology* **47**(11), 61-68.

Westerhoff, P., Song, R., Amy, G. and Minear, R. (1997) Applications of ozone decomposition models. *Ozone-Science & Engineering* **19**, 55-73.