Modeling the fate of hazardous compounds in conventional wastewater treatment within a waste minimization framework

A.S. Mayer, V.J. Wildfong & R.A. Voigt

Department of Geological Engineering, Geology and Geophysics, Michigan Technological University, Houghton, MI 49931-1295, USA

Abstract

The objective of this work is to develop a modeling tool for predicting the impacts of waste minimization measures on wastewater pollution control. The modeling tool focuses on predicting the fate of volatile organic chemicals (VOCs) in primary and secondary wastewater treatment. The VOC fate model is linked to an existing wastewater treatment model for predicting biological oxidation in activated sludge systems. The VOC fate/wastewater treatment model is incorporated into a process flowsheet simulator package for modeling the fate of VOCs produced from simulated industrial processes, allowing for assessment of waste minimization schemes.

1 Introduction

An important factor in determining which wastes should be targeted for minimization is the treatability of the waste. Wastes that are easy to treat, or are beneficial to the treatment of other wastes, may not be the most suitable wastes for targeting. VOCs are a class of hazardous compounds which are currently a major focus of waste minimization efforts. The fate of VOCs released into the influent of municipal wastewater treatment plants is an important component of hazardous waste fate and treatability assessment. Accurate modeling of VOC fate in conventional wastewater treatment
must take into account at least four removal mechanisms: biodegradation, sorption, stripping, and volatilization. There are several comprehensive process fate models that attempt to predict contaminant removals (c.f. Baillod et al.). However, these models all have shortcomings, including oversimplified conceptual approaches, limited choices for wastewater treatment processes, or the inability to correct for variations in operating parameters. The first objective of this work is to develop a model for predicting VOC fate in conventional wastewater treatment plants.

Process simulator flowsheet (PSF) software is used in the chemical processing industry to simulate the behavior of unit or multiple chemical production processes. Incorporation of waste treatment models into PSFs would allow the connection of a conventional wastewater treatment model to an effluent wastewater stream which is emitted from an industrial process. The combination of the PSF and the treatment model can be used to analyze the effects of waste minimization measures on the ultimate fate of toxic compounds which are produced in liquid waste streams. Furthermore, incorporation of treatment models into a flowsheet simulator would allow the industrial community to utilize a treatment model within a familiar software package. The second objective of this work is to incorporate the VOC fate model into a widely-used PSF.

2 VOC Model Development

The following operations were included in the VOC fate model: weirs and drops, aerated grit chamber, primary clarifier, aeration basin, and secondary clarifier. Figure 1 illustrates the model configuration and the conceptual removal mechanisms—biodegradation, sorption, stripping, and volatilization—for each unit operation. Other removal mechanisms such as photolysis, hydrolysis, or other abiotic reactions are considered to be negligible. VOC biodegradation is caused by biochemical reactions involving microorganisms in the activated sludge system. The rate of disappearance is modeled as a first order reaction, since VOCs usually are present in low concentrations at treatment plants:

\[ r_b = k_b XCV \]
Figure 1. Schematic of VOC Fate Model, including unit processes and removal mechanisms.
where \( r_b \) is the removal rate due to biodegradation, \( k_b \) is the biodegradation rate constant, \( X \) is the biomass concentration, \( C \) is the VOC concentration, and \( V \) is the tank volume.

Sorption is modeled as an equilibrium process, using a linear Freundlich isotherm\(^3\). The VOC removal rate due to sorption, \( r_s \), is then given by

\[
    r_s = Q_w X_w K_p C
\]

where \( K_p \) is the solid-liquid partition coefficient, which may be determined from correlations with octanol-water partition coefficients \( (K_{ow})^3 \); \( Q_w \) is the sludge wastage rate; and \( X_w \) is the concentration of suspended solids.

VOCs can be removed from the wastewater treatment facility by wind-induced volatilization into the atmosphere from surfaces of open water bodies. The rate of removal by volatilization, \( r_v \), is given by (assuming that the air above the basin has a negligible VOC concentration)

\[
    r_v = K_{la} CV
\]

where \( K_{la} \) is the overall mass transfer coefficient. The value of \( K_{la} \) can be determined from a two-film expression which incorporates correlations for liquid and gas phase mass transfer coefficients, which in turn depend on the wind speed and gas and liquid phase Schmidt numbers\(^4\). The VOC mass transfer coefficient also can be calculated by adjusting the oxygen mass transfer coefficient\(^5\).

Stripping in wastewater treatment facilities occurs when a gas phase is introduced into the process water due to water agitation or air bubbles that are mechanical in origin. Stripping can occur by surface or bubble aeration in the activated sludge aeration basin or at weirs and drops. If the aeration basin is assumed to be uncovered, the rate of removal due to stripping by surface aeration is given by equation (3). Calculation of \( K_{la} \) for surface aeration is based on \( K_{la} \) expressions derived for oxygen transfer in aeration basins, adjusted by the ratio of VOC and oxygen diffusivities\(^6\). For diffused-bubble aeration, the removal rate, \( r_{sb} \), is given by\(^7\)

\[
    r_{sb} = Q_g HC \left( 1 - e^{-\phi} \right)
\]
where $Q_g$ is the aeration basin gas flow rate, $H$ is Henry's constant, and $\phi$ is an equilibrium correction term, which is based on a $K_{1a}$ value and an effective depth where equilibrium between the gas and liquid phases is reached. The value of $K_{1a}$ is based on the $K_{1a}$ for oxygen, which must be adjusted to account for the nature of the tests used to determine the oxygen $K_{1a}$ in diffused-bubble aeration. Stripping at weirs and drops can be modeled either with plug flow conditions for the liquid and completely mixed conditions for the gas, or the reverse. The removal rates for these conditions are based on the flow rates, configurations and the liquid-gas mass transfer rates for the weir or drop^8,9. The VOC mass transfer rates are adjusted from measured oxygen mass transfer rates.

Mathematical representations of the conceptual removal mechanisms were incorporated into mass balances for each unit operation. All of the unit processes are modeled as single completely stirred reactors (CSTRs), except for the activated sludge aeration basin. The activated sludge aeration basin can be simulated as series of completely stirred reactors to account for varying degrees of plug flow or variations in basin configurations. The complete set of mass balance equations included in the model is too large to be described here, but an example of mass balance equation is given as follows, for the primary clarifier.

$$Q_{i2}C_{i2} = (Q_o2C_{o2}) + (Q_{w2}X_{w2}K_{p2}C_{o2}) + ([K_{1a}]_2V_2C_{o2})$$  \(5\)

where the subscripts 2, i and o represent the primary clarifier unit process, influent, and effluent, respectively.

Model executions consist of input of operational, environmental, and physico-chemical parameters, output of VOC removal percentages for each mechanism and unit process, and output of effluent concentrations for each unit process. The model was designed to be used in conjunction with the Simulation of Single Sludge Processes (SSSP) biological treatment simulation model\textsuperscript{10}. Mass balances from SSSP provide values of biomass concentrations, $X_b$, and sludge wastage rates, $Q_{wb}$, for the activated sludge basin. The VOC concentration in the wastewater stream is assumed to have no effect on the activated sludge process. The SSSP model is executed independently of the VOC fate model and the values of $X_b$ and $Q_{wb}$ are used as input for the VOC fate model.
3 Application of VOC Model

Results from VOC model simulations were used in comparisons to existing models, comparisons to wastewater treatment plant effluent data, and a sensitivity analysis. The VOC model was compared to results from six existing models (see Baillod et al.\textsuperscript{1} for descriptions of existing models) by conducting simulations with a single parameter set. The parameter set and the results from the existing models are found in Baillod et al.\textsuperscript{1}. In most cases, the models produced similar results; however, there are several significant discrepancies between some model simulation results. These discrepancies were attributed either to differing mathematical representations of removal mechanisms or parameter changes due to calibration of the existing models.

A validation study was conducted by comparing model output to a plant study of three treatment facilities\textsuperscript{11}. The model output agreed reasonably well with the plant data, but did not match some of the removal percentages. The situations where the model did not match the plant data may be explained by the facts that the plant data contained a large amount of variability and often lacked values for important parameters needed for accurate simulation. It was found that single sorption correlations could not accurately predict VOC removal by sorption over the entire range of $K_{ow}$ values.

Model sensitivity analyses identified the parameters which influence particular VOC removal mechanisms. The dominant removal mechanism is strongly dependent on physico-chemical properties of the particular VOC. In general, volatilization was the least significant removal mechanism. Removal by biodegradation is sensitive to biodegradation rate constant, basin volume, and biomass concentration. Removal by stripping is sensitive to changes in temperature, wind speed, and aeration basin gas flow rate. Surface aeration is sensitive, but diffused-bubble aeration is insensitive to changes in the correction factor for process water relative to clean water. Removal by sorption is sensitive to the sludge wastage rate. Significant removal by stripping can occur at weirs or in aerated grit chambers. Modeling the aeration basin as a series of CSTRs instead of as a single CSTR simulates increased overall removal because plug flow is approached. Step feed operation simulations exhibited decreased VOC removal, when compared to configurations
where all of the secondary treatment influent was directed to the first aeration basin.

4 Incorporation into Process Simulator Flowsheet

The ASPEN PLUS\textsuperscript{12} simulator is a unit operation-driven PSF. It is widely used in industry for plant design and optimization, has a sophisticated and robust simulator, can incorporate user-defined FORTRAN programs, and offers a high degree of adaptability. An ASPEN PLUS input code was constructed to satisfy necessary system inputs and to enable a subroutine call. A single mixing unit operation which considers only a liquid phase was established to set-up the user model subroutine. This subroutine call links a modified version of FORTRAN code for the VOC fate model to the ASPEN PLUS system. Minor modifications were made to the FORTRAN code to conform to ASPEN PLUS requirements. The ASPEN PLUS input code was able to successfully call the FORTRAN code for the VOC fate model, and access external input data files. The output is produced either in ASPEN PLUS or an external output data file. At this point, an industrial process can be built using conventional ASPEN PLUS procedures and the waste stream produced from the industrial process can be sent to the VOC fate model. The combination of the PSF and the treatment model can be used to analyze the effects of waste minimization measures on the ultimate fate of VOCs which are produced in liquid waste streams.

5 Conclusions

A model for predicting the fate of VOCs in conventional wastewater treatment plants was developed. Model results compared favorably to wastewater treatment plant data and existing VOC fate models. The model was used analyze the sensitivity of VOC removal to physico-chemical properties, environmental parameters, plant operation parameters, and plant configurations. The model was successfully incorporated into a PSF, which allows for the analysis of waste minimization schemes with regard to the ultimate fate of VOCs in liquid waste effluents.

Acknowledgement

This work has been funded by the Michigan Technological University/U.S. Environmental Protection Agency Center of Excellence.
References


