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TREATMENT SYSTEM RESPONSE TO TRANSIENT AOX (ADSORBABLE ORGANIC HALOGEN) LOADINGS

D. A. Barton*, J. D. Woodruff**, T. M. Bousquet*** and A. M. Parrish***

* *National Council for Air and Stream Improvement, Inc., Medford, MA 02155, USA*
** *Department of Civil and Environmental Engineering, Tufts University, Medford, MA 02155, USA*
*** *National Council for Air & Stream Improvement, Inc., Corvallis, OR 97339, USA*

ABSTRACT

If promulgated as proposed, effluent guidelines for the U.S. pulp and paper industry will impose average monthly and maximum daily numerical limits of discharged AOX (adsorbable organic halogen). At this time, it is unclear whether the maximum-day variability factor used to establish the proposed effluent guidelines will provide sufficient margin for mills to achieve compliance during periods of normal but variable operating conditions within the pulping and bleaching processes. Consequently, additional information is needed to relate transient AOX loadings with final AOX discharges. This paper presents a simplistic dynamic model of AOX decay during treatment. The model consists of hydraulic characterization of an activated sludge process and a first-order decay coefficient for AOX removal. Data for model development were acquired by frequent collection of influent and effluent samples at a bleach kraft mill during a bleach plant shutdown and startup sequence. © 1997 IAWQ. Published by Elsevier Science Ltd.

KEYWORDS

Activated sludge treatment; AOX; bleached kraft mill; dynamic modeling; hydraulic modeling

INTRODUCTION

Dynamics in daily operating conditions at bleached kraft mills result in non-steady state loadings of AOX (adsorbable organic halogen) discharged to the wastewater treatment plant. Variability factors derived during the development of effluent guideline standards are intended to accommodate this expected variability. However, the AOX maximum-day variability factor initially proposed by EPA ($VF_{99} = 1.863$) is based on an extremely limited data set. A previous NCASI study (NCASI, 1994) calculated AOX maximum-day variability factors ranging from 1.38 to 2.60 for eleven mills.

Mills which may be able to achieve the long-term average AOX limitation but experience effluent quality variability exceeding that upon which the maximum-day limit is based, may seek to alter bleach plant operating conditions to attempt to reduce AOX loading variability. To project the impact which reduced AOX loading variability will have on final effluent variability, a dynamic (time-varying) model of the wastewater treatment process is needed. Conversely, the availability of such a model could provide a tool to estimate the maximum AOX loading variability which will allow for compliance with maximum-day limitations.

Development of a dynamic model requires a data set consisting of frequent data points acquired during a period of transient conditions. The current study collected influent and effluent data, at intervals as frequent as every two hours, prior to, during, and following a twelve hour mill shutdown. Collection of conservative parameters (conductivity and, although not always truly conservative, color), as well as AOX data, allows for the establishment of system hydraulics and AOX removal kinetics.

METHODS

The study consisted of two phases; (a) sample collection and analysis and (b) wastewater treatment process modeling.

Sample collection and analysis

Sample collection was performed at a bleached kraft mill with a wastewater treatment process consisting of; pH adjustment mix tank, traveling screens pretreatment, primary clarification, activated sludge aeration basins, and secondary clarifiers. The activated sludge aeration basins include a "plug-flow" section followed by a "complete-mixed" basin. Sample collection points were immediately prior to the traveling screens (influent) and at the final effluent prior to discharge to the receiving stream. Two non-process waste streams, contributing approximately ten percent of the total flow, enter the treatment plant at points downstream of the influent sample.

Sample collection was coordinated with a planned mill shutdown/startup sequence, originally scheduled for a 24 hour period. Commencing with the beginning of the shutdown, influent and effluent grab samples were collected every two hours until approximately 16 hours after resumption of normal bleach plant operations. The study plan called for two 24-hour composite samples prior to shutdown. However circumstances at the mill resulted in the shutdown occurring one day earlier than expected, thus allowing for collection of only one 24-hour composite. In addition, the duration of the shutdown was shortened to 12 hours. After bleach plant startup a sequence of three 8 hour composite samples (composites of 3 to 4 grab samples) followed by five days of 24-hour composites (influent: composite of twelve 2-hour grab samples, effluent: automatic composite sampler) were collected.

Samples were preserved with nitric acid to pH 3.0-3.2 and shipped to NCASI for subsequent analysis. An aliquot of the sample was filtered using 0.7 μm glass fiber filters for conductivity and color (absorbance at 465 nm) determinations. The remaining portion of the sample was analyzed for AOX at the NCASI West Coast Regional Center by Method 506 (APHA *et al.*, 1989).

Wastewater treatment process modeling

Modeling was performed using a spreadsheet-based approach with each row of the spreadsheet representing a discrete time extending over the interval of the sampled data. Numerical integration was performed using a simple finite difference approach with time steps of 0.2 and 0.25 hours during the transient (shutdown/startup) and stable operation periods, respectively. Each of four major units of the treatment process (primary clarification, plug-flow aeration basin, complete-mixed aeration basin, and secondary clarification) were considered in sequence. Hydraulic characterization of the unit processes was based on a combination of theoretical ideal mixing conditions (e.g., plug-flow or complete-mixed) and empirical observations reported by others. The hydraulic model performance was evaluated against the conductivity data collected during the mill shutdown/startup. Hydraulic model verification was performed using color data.

The hydraulic model was then used to estimate an AOX decay rate. AOX removal was assumed to occur only in the activated sludge aeration basins. The extent to which alkaline hydrolysis may have contributed to the observed reduction in AOX across the treatment plant could not be quantified in this analysis.

HYDRAULIC CHARACTERIZATION

Unit process hydraulics

Table 1 presents the design parameters and the assumptions made in this study relative to the mixing regime within each process unit. Each stage of the treatment process consists of duplicative units (e.g., two primary clarifiers). The primary clarifiers were modeled as a plug-flow system assuming the actual detention time was one-half of the design detention time. These rather simplistic assumptions were made in light of limited hydraulic characterization data for primary clarifiers and because of the short detention time of the clarifiers (design detention time = 1.2 hours). The latter was found to cause the model results to be relatively insensitive to the hydraulic conditions assumed for these units.

Table 1. Hydraulic characterization of unit processes

Process Unit	Design Detention Time (hrs.)	Hydraulic Characterization
Primary clarification	1.2	Plug-flow; ½ design detention time assumed
"Plug-Flow" aeration basins	1.8	Two complete-mix tanks-in-series; Design detention time
"Complete-Mix" aeration basins	2.4	Complete-mix basin; design detention time
Secondary clarification	11.1	Plug-flow with dispersion; ½ design detention time with peak at ½ of actual detention time

The "plug-flow" aeration basins form a ring around the circular "complete-mix" basin and thus exhibit a high length-to-width ratio. This configuration can be simulated by a multiple tank-in-series approach. In this study, the use of two complete-mix basins in series provided satisfactory fit to the observed data. Returned activated sludge (RAS) flow from the secondary clarifiers, with a concentration assumed to be equal to the final effluent, was routed to the first aeration basin. The "complete-mix" aeration basins are well mixed (greater than 40 m^3 air/min•1000 m^3) and therefore can be simulated by a single complete-mix basin.

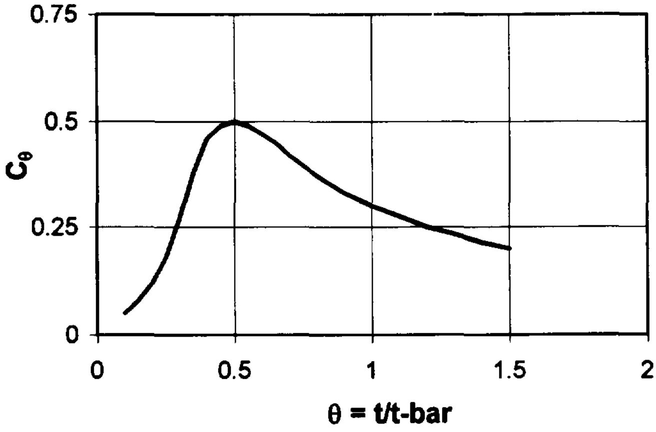

Figure 1. Residence distribution profile for secondary clarifier.

The secondary clarifiers account for 79 percent of the total nominal detention time of the wastewater treatment process. Thus, accurate portrayal of the non-ideal mixing conditions of these units is needed for successful modeling of the treatment plant hydraulics. Data provided elsewhere for kraft mill clarifiers (Bors and Robinson, 1980, Sackellares *et al.*, 1984) suggest that the effective volume (i.e., fluid transport zone) can account for approximately one-half of the total clarifier volume and that the time to peak of a conservative tracer (dye) occurs at one-quarter to one-half of the actual mean residence time. Figure 1 depicts a residence time distribution (RTD) with the peak occurring at one-half of the actual residence time.

To map the continuous RTD to the discrete time intervals of the spreadsheet model, effluent concentrations under the non-ideal flow conditions were simulated by applying weighting factors to three elements of the time series entering the clarifier using the following expression:

$$C_{OUT\,(T)} = \alpha_1\, C_{IN\,(T - 0.5t)} + \alpha_2\, C_{IN\,(T - t)} + \alpha_3\, C_{IN\,(T - 1.5t)}$$

where the α values sum to unity and t is the estimated actual detention time of the clarifier. Values of α yielding the minimum sum of squares of the residuals were found to be 0.5, 0.3, and 0.2 for α_1, α_2, and α_3, respectively.

Model calibration data

Influent and effluent conductivity and color data were used to evaluate the hydraulic model. Data were interpolated at the time intervals indicated above. Data for the first 24 hours and for the period between 64 and 168 hours were collected as composite samples. Although conductivity is expected to be a conservative parameter, the average effluent conductivity was found to be approximately 400 μmhos less than the average influent value. This difference was attributed to one of the non-process waste streams bypassing the influent sample collection point and effluent conductivity values were adjusted accordingly. Effluent UV absorbance (color) and AOX concentrations were reduced in proportion to the bypass and total mill flow.

Hourly flow data to each of the two secondary clarifiers, as well as RAS flow from each clarifier, was provided by the host mill. Clarifier flow rates were averaged into eight periods of relatively constant flow, with flow rates ranging from 66 m^3/min (17500 gpm) during the 12-hour shutdown to a maximum of 91 m^3/min (24000 gpm) during a 5-hour event occurring three days after the shutdown. The average flow for the seven day period was 75 m^3/min (19800 gpm).

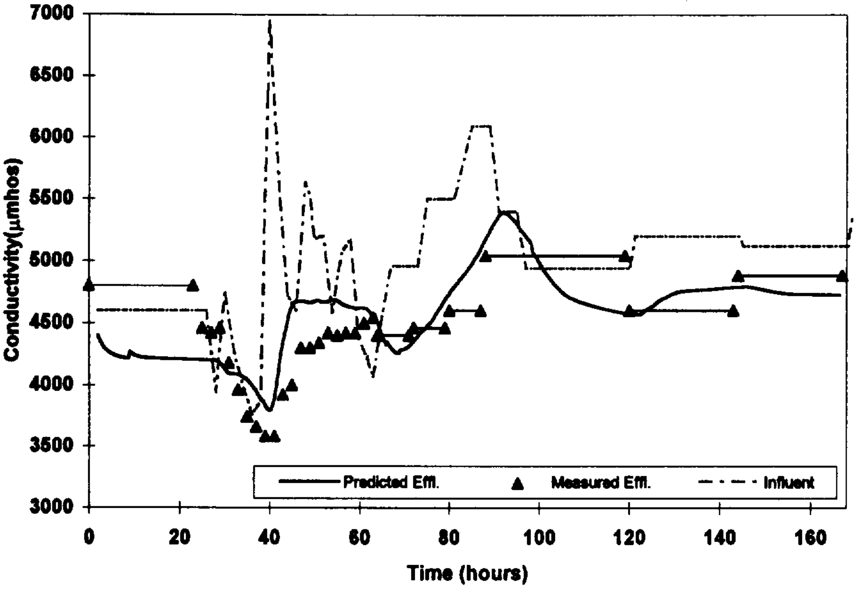

Figure 2. Comparison of predicted and measured conductivity.

Hydraulic model results

Figure 2 contrasts the predicted effluent conductivity with the measured data. Horizontal bars in the figure represent composite samples. Initial conditions for each unit process were set equal to the 24-hour composite influent sample conductivity (4600 μmhos) less the 400 μmhos adjustment. The large residual between predicted and measured conductivity over the initial 24 hours may result from (a) the effects of sample compositing (i.e., effluent conductivity may have experienced a downward trend during the 24-hour compositing period with only the latter portions of the period being related to the measured influent conductivity level) and (b) the 400 μmhos adjustment may not have been appropriate for this time interval.

After the initial 24 hour period, the profile of the predicted effluent conductivity generally follows that of the measured data. During the bleach plant shutdown the model over-estimated the minimum measured effluent conductivity value (simulation hour 40) by approximately 300 μmhos. The effluent response during bleach plant startup was also somewhat over-estimated by the model. Maximum residuals reach 675 μmhos at hour 45. Adjustments to the secondary clarifier alpha values and the number of tanks-in-series assumed for the plug-flow aeration basins were not successful in improving the model fit for this time interval of the simulation.

Confirmation that an appropriate hydraulic model had been developed was made by applying the conductivity-based hydraulic conditions to the influent and effluent time series for color (expressed as UV absorbance). As displayed in Figure 3, reported influent UV absorbances fluctuated widely and were consistently greater than corresponding effluent measurements. Nonetheless, the model effectively dampened the short-term influent variability and the agreement between predicted and measured effluent absorbance during and immediately following the bleach plant shutdown is reasonably good. An extended period of relatively low effluent UV absorbance (hour 50 to hour 80) could not be accounted for by the model based on the influent data. From this period onward, the residuals between predicted and measured absorbances are relatively low (less than 30 percent of the mean measured effluent absorbance).

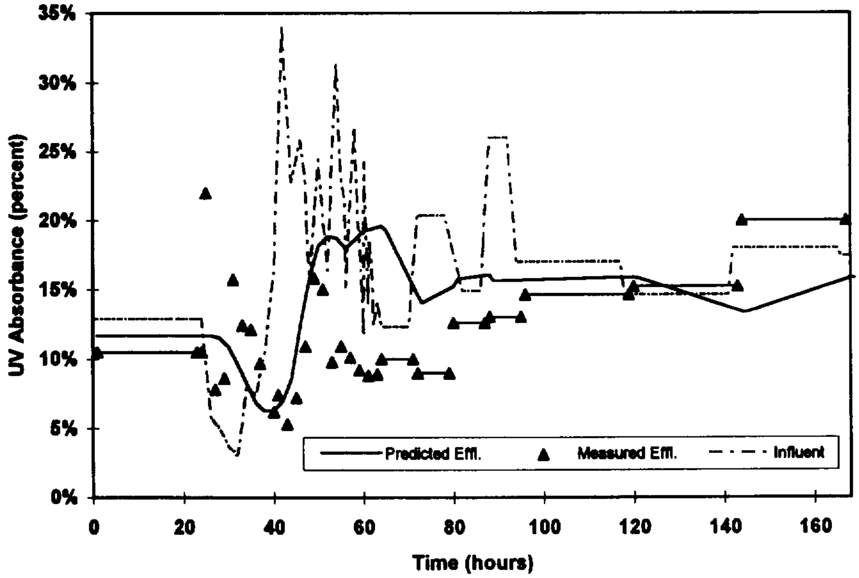

Figure 3. Comparison of predicted and measured UV absorbance.

AOX REMOVAL MODEL

Transient effluent AOX concentrations were simulated by applying the hydraulic model presented in the previous section and incorporating a first-order decay coefficient to account for AOX degradation occurring within the treatment process. The decay term was invoked in the aeration basin (plug-flow and complete-mix) components of the model only. Effluent AOX from each of these unit processes was calculated for each time interval by the following expression:

$$AOX_{T+\Delta T} = AOX_T + \Delta T * [\,(Q/V)*(AOX_{INF} - AOX_T) - k_{AOX}*AOX_T\,]$$

where AOX_{INF} is the effluent AOX from the preceding unit process and k_{AOX} is in units of time $^{-1}$.

The value of k_{AOX} was varied until the sum of squares of the residuals during the interval of 20 hours to 120 hours was minimized. After this period, the extended compositing period over which the AOX samples were collected makes it difficult to simulate transient conditions. A k_{AOX} value of 0.3 hr $^{-1}$ was found to yield the best model fit to the observed data. These results are displayed in Figure 4. Maximum residuals between predicted and measured data are less than 35 percent of the mean effluent AOX concentration during the evaluation interval.

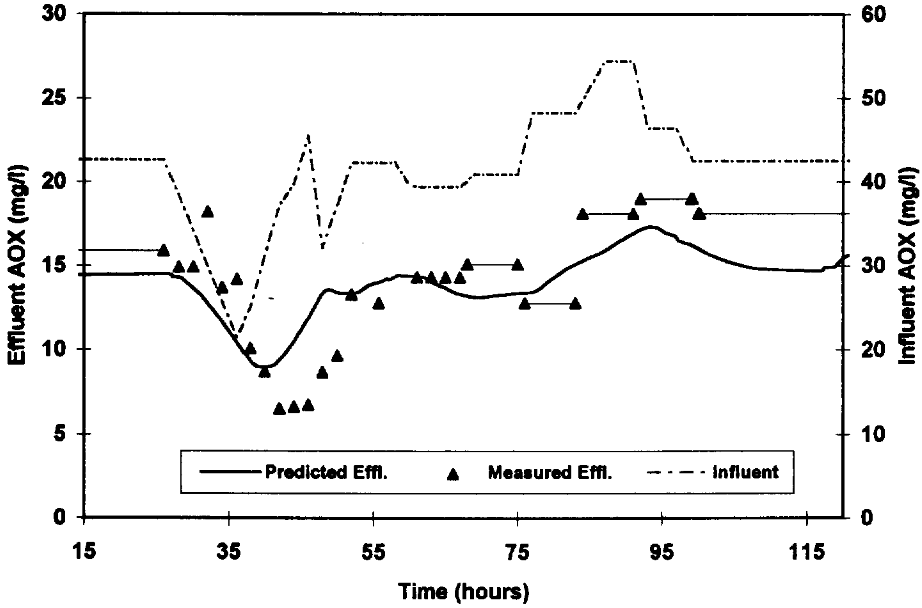

Figure 4. Comparison of predicted and measured AOX ($k_{AOX} = 0.3$ hr $^{-1}$).

DISCUSSION

The k_{AOX} value determined in this analysis is likely specific to the treatment conditions of the mill under study and should not be interpreted as a "typical" AOX removal rate. Rather, the methodology developed in this study is intended to serve as a model for estimating AOX removal rates in bleached chemical pulp mill effluent treatment processes. An indication of the sensitivity of the selected k_{AOX} value on the predicted effluent AOX concentration at the host mill is illustrated in Figure 5.

It is important to recognize that the observed degradation of AOX is likely not entirely attributable to biodegradation. Rather, chemical dehalogenation presumably accounts for a portion of the AOX degradation. Chemical reaction may take place in the primary clarifiers (although at this mill the short detention time of the primary clarifiers suggests the extent of degradation in these units would be relatively small), in the aeration basins (concurrently, or perhaps competitively, with biodegradation) and in the final clarifiers. Previous NCASI studies have shown that between approximately 20 to 50 percent of chlorine/chlorine dioxide stage effluent AOX may degrade abiotically through pH adjustment to 7 when held for 24 hours at 38°C (NCASI, 1996). Studies are in progress to better define the relative influence of chemical and biological AOX degradation mechanisms.

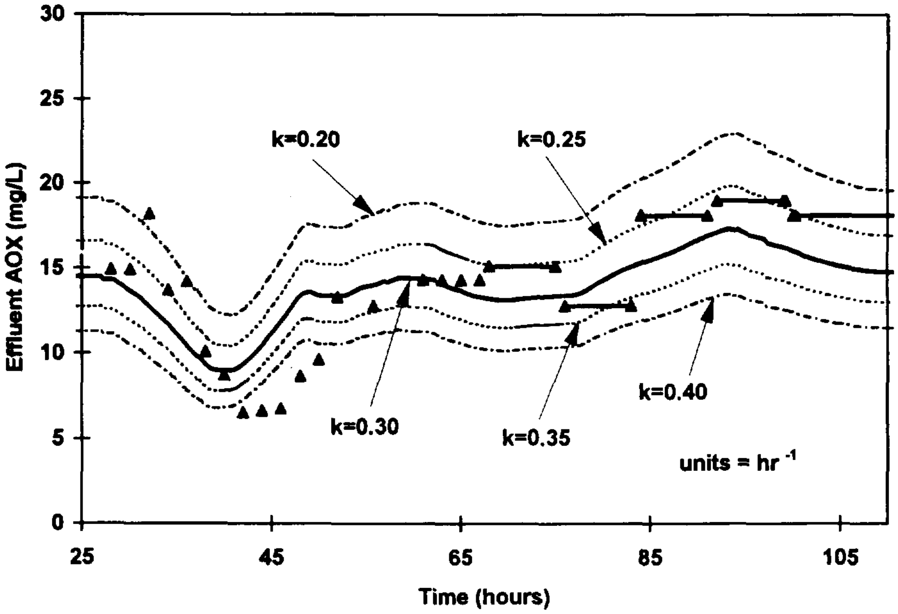

Figure 5. Sensitivity analysis of k_{AOX} on predicted effluent AOX.

If a satisfactory model of AOX removal is developed, it may be possible to establish the maximum variability in AOX generation rate for a given mill to maintain AOX compliance. For example, if the long-term average and degree of autocorrelation of a time series of bleach plant AOX loadings is known, such a model could be used to determine the largest standard deviation of the time series data (i.e., variability) for which effluent AOX compliance can be achieved. Currently available influent AOX loadings data sets are very limited in nature, thus it may not be feasible to characterize the necessary loading parameters at this time.

CONCLUSIONS

Wastewater treatment plant hydraulics can be adequately simulated using a fairly simplistic approach consisting of a sequence of individual unit processes under various mixing conditions. The availability of conservative tracer data collected during transient conditions enhances the degree of model refinement possible. Applying the hydraulic model to influent and effluent AOX data collected at an activated sludge process treating wastewaters from a bleached kraft mill resulted in a first-order AOX degradation coefficient of 0.3 hr^{-1}.

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