DETERMINATION OF BIOLOGICAL KINETIC CONSTANTS USING RESPIROMETRY FOR THE WATER9 AIR EMISSIONS MODEL

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ABSTRACT

The U.S. E.P.A. Water9 air emissions model can be used to estimate air emissions, biological removal and adsorption of organic compounds in wastewater treatment and collection systems. Although the model contains an extensive database of physical property data and biological treatment kinetic constants for organic compounds, the Water9 documentation recommends that site-specific biotreatment kinetic data be used whenever available.

The Water9 model uses a zero-order substrate removal constant (K_{max}) and a first-order substrate removal constant (K_1). While these appear similar to, and have the similar units as, the Monod maximum substrate removal constant q_{max} and the quotient of the Monod q_{max} divided by the half-saturation factor (K_s), the procedures given for determining the Water9 kinetic factors by batch testing (40CFR Part 63 Appendix C) indicate that there are important differences. The Water9 factors are based on the entire biomass population as measured by the mixed liquor suspended solids, while the intrinsic Monod kinetics are based on the active biological population only. In addition, an effective K_1 is determined at the substrate concentration of interest, rather than being a more generally applicable intrinsic constant.

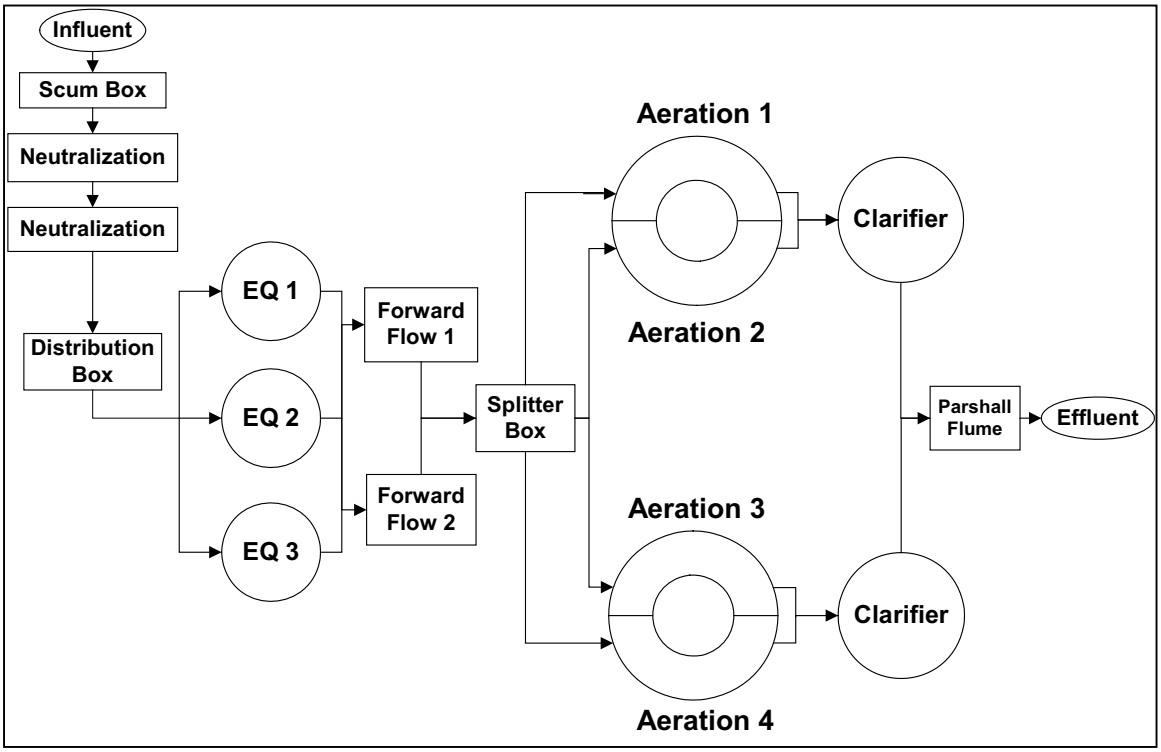
Water9 modeling of styrene emissions from an industrial biological wastewater treatment system using the default physical property and kinetic data gave estimated effluent concentrations and air emissions considerably greater than indicated by effluent analytical data, and as indicated by the lack of any styrene odor at the treatment plant. Batch respirometry testing using biomass from the industrial plant and pure styrene as the substrate was used to generate a styrene removal profile based on Monod kinetics. The substrate removal profile was used in place of substrate analytical data in a modification of one of the recommended procedures for determining the Water9 kinetic constants. Using the site-specific biorate constants resulted in estimates of the styrene effluent concentrations in much better agreement with measured concentrations in the plant effluent. The styrene air emissions estimated by the model decreased by several orders of magnitude.

KEYWORDS
Respirometry, Water9, air emissions, kinetic constants

INTRODUCTION

The Rohm and Haas plant located in Bristol, PA produces a variety of polymer products, including emulsion polymer coatings, solution polymers and digital imaging products. Wastewater from the production units is treated in a 1.5 million gallon per day wastewater treatment plant (WWTP) by equalization, neutralization and biological treatment. The WWTP was designed and built to minimize odors, with all tanks up to the secondary clarifiers covered. A flow diagram of the plant is shown in Figure 1.

Figure 1. Bristol WWTP



WATER9 MODEL

The Water9 model was developed to estimate air emissions from wastewater treatment collection and treatment systems. The fraction of each organic compound in wastestreams that is emitted to air, removed biologically, adsorbed or that remains in the system exit streams is calculated by mass balance and mass transfer calculations for each treatment unit based on the model unit parameters and the properties of each chemical. The Water9 model is available for download from the US EPA web site at http://www.epa.gov/ttn/chief/software/water/index.html .

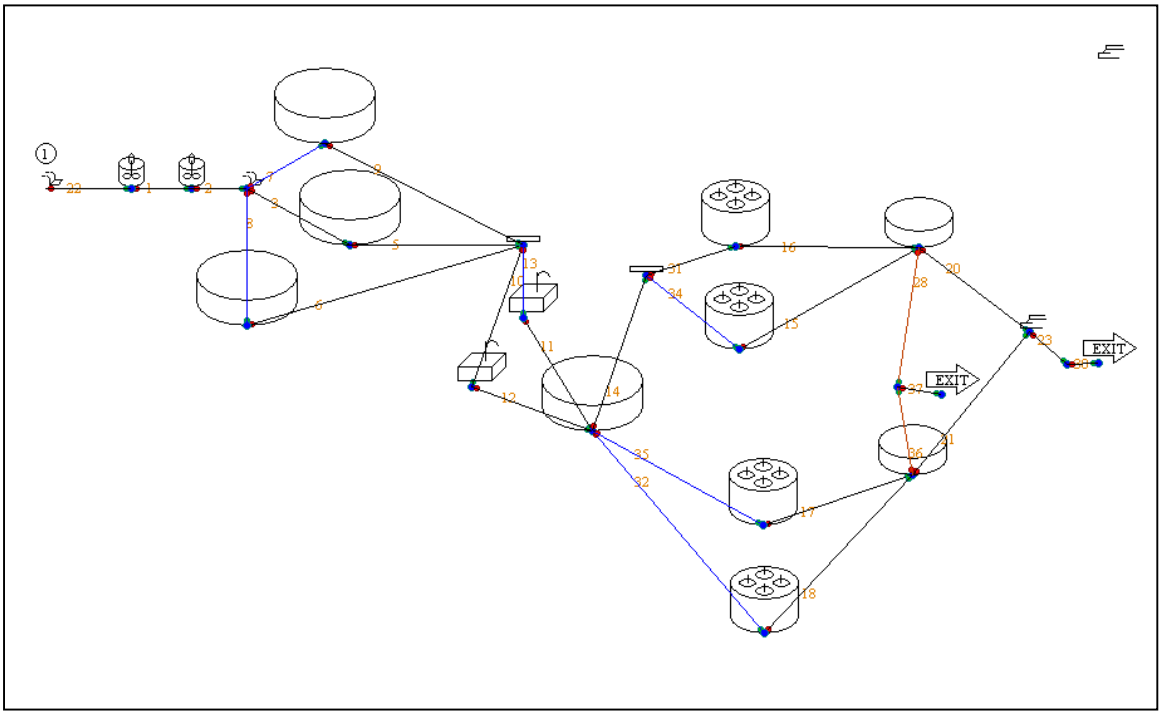
The model contains modules for approximately 50 wastewater treatment and conveyance units and an extensive database of physical property data and biotreatment kinetic constants for organic compounds. Although default biotreatment kinetic constants and the ability to generate constants from molecular structure are provided, the Water9 documentation recommends using site-specific biodegradation constants whenever they

are available. The reference for procedures for determining the kinetic constants is 40 CFR Part 63 Appendix C, Determination of Fraction Degraded (Fbio) in a Biological Treatment Unit.

PRELIMINARY WATER9 MODELING RESULTS

Personnel at the plant wished to improve the method of estimating emissions from the wastewater treatment tanks for reporting required by the site air permit and for Toxic Release Inventory reporting. A Water9 model of the WWTP was developed and influent data for 21 organic compounds detected in the plant influent waste streams was entered into the model. The Water9 flowsheet for the plant is shown in Figure 2 and Table 1 contains the list of compounds in the plant wastewater.

Figure 2. Water9 Flowsheet of the Bristol WWTP Model



With the exception of styrene, Water9 results using default physical properties and kinetic constants were in reasonable agreement with plant measured effluent concentrations and previous estimations of air emissions. Estimated emissions of styrene were an order of magnitude larger than the combined emissions of the other 20 chemicals, and the predicted effluent concentration, 1200 µg/L, was much greater than the measured concentrations of <1-5 µg/L.

The Water9 physical property data for styrene was reviewed and compared to literature and company data sources. While alternate values were found for Henry's Law

Table 1. Organic Compounds in Bristol WWTP Water9 Model

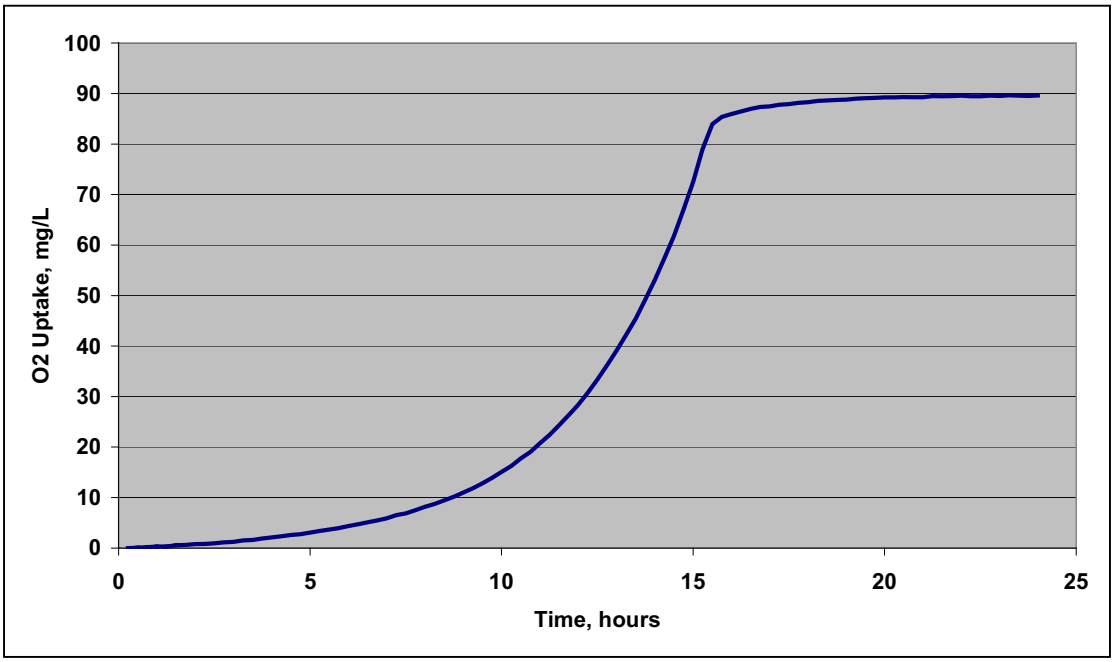
1 butanol	ethyl acrylate
methyl ethyl ketone	2-ethylhexylacrylate
ethylbenzene	formaldehyde
tert-butanol	methacrylic acid
acetaldehyde	methanol
acrylic acid	methyl acrylate
acrylonitrile	methyl methacrylate
benzene	styrene
butyl acrylate	toluene
butyl methacrylate	xylene
chloroform	

Constants, octanol-water partition coefficients and other parameters, use of the alternate values had little or no effect on predicted emissions. It was concluded that the biological removal coefficients were underestimating the amount of biological removal occurring in the system.

RESPIROMETRY TESTING USING STYRENE

In order to determine site-specific biodegradation rates for styrene, closed-bottle respirometry using a Challenge Environmental Systems Respirometer was performed using styrene as the substrate and with biomass from the plant biological treatment system. The oxygen uptake for a respirometry run fed 100 mL/L of styrene is shown in Figure 3.

Figure 3. Measured Oxygen Uptake from Respirometry with 100 mL/L Styrene Feed



The data was curve fit to the Monod model

$$\mu = \frac{\mu_{max} S}{K_s + S}$$

where μ = cell growth rate, hr^{-1}
μ_{max} = maximum cell growth rate, hr^{-1}
S = substrate concentration, mg/L
K_s = half saturation constant, mg/L.

The Monod model can also be expressed in terms of the substrate removal rate, q

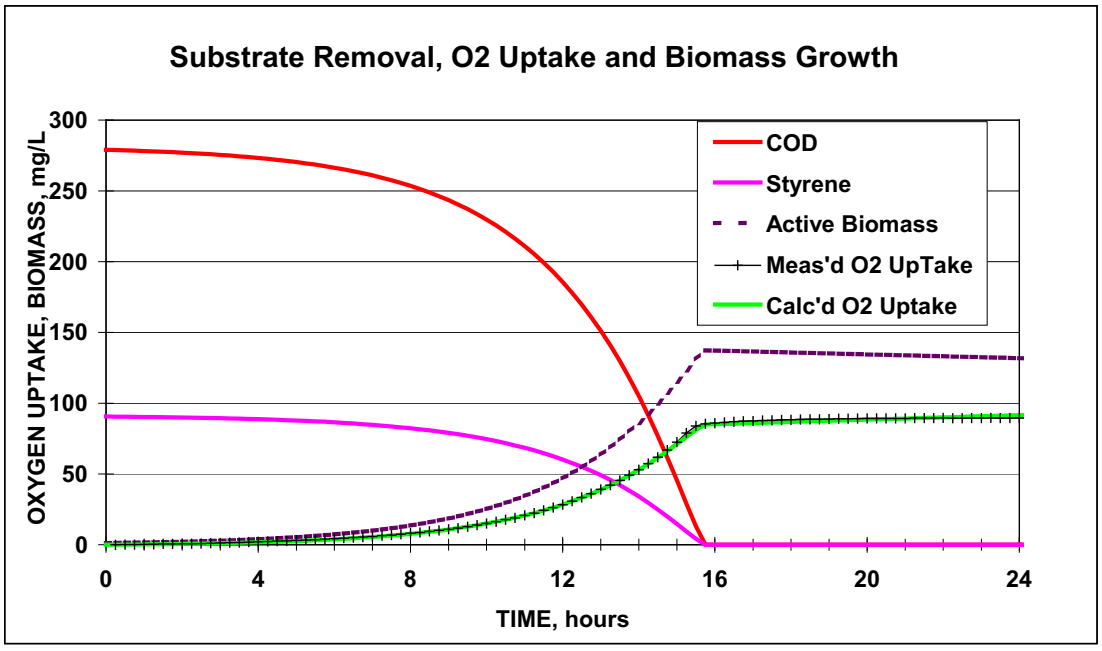
$$q = \frac{q_{max} S}{K_s + S}$$

where q = substrate removal rate, hr^{-1}
q_{max} = maximum substrate removal rate.

While "K" is sometimes used for the Monod substrate removal rate, "q" is used here to differentiate the values from the Water9 constants. The Monod q and μ are related by the growth yield coefficient, Y_g, which is μ/q. At low substrate concentrations, the above equation would approach a first-order reaction, with $q = q_{max} S / K_s$ and first-order constant $q_1 = q_{max} / K_s$.

The results of the fitting of the respirometry data to the Monod model are shown in Figure 4, in which the measured oxygen uptake and the modeled oxygen uptakes, cell growth and substrate reduction (as Chemical Oxygen Demand and as styrene) are plotted against time.

Figure 4. Monod Kinetics Growth and Substrate (Styrene) Removal



The Water9 model uses biorate constants K_{max} and K_1, with $K_1 = K_{max}/K_s$. While the constants had similar names and units to the Monod constants, the Water9 constants are based on the aggregate mixed liquor volatile suspended solids (MLVSS) as a surrogate for the total biomass concentration, rather than the portion of the biomass actively growing with a particular substrate. The active portion of the biomass treating a mixed substrate typically ranges from 5-25%, with the portion active for a particular chemical substrate being only a fraction of the total active biomass. In addition, in the procedure for determining the Water9 constants using a batch test, K_1 is determined at a specific substrate concentration, rather than as a more general system constant. Table 2 below shows a comparison of the Monod and Water 9 kinetic constants.

Table 2. Monod and Water9 Kinetic Constants

Model	Constants	Definition	Units
Monod	μ_{max}	maximum cell growth rate	hr^{-1} (mg cells/mg cells-hr)
	q_{max}	maximum substrate removal rate	hr^{-1} (mg substrate/mg cells-hr)
	K_s	half-saturation constant	mg substrate/L
Water9	K_{max}	maximum substrate removal rate; zero-order rate constant	mg substrate/g biomass-hr
	K_1	first-order rate constant	L/g biomass-hr

RECOMMENDED PROCEDURES FOR DETERMINATION OF WATER9 BIOLOGICAL REMOVAL KINETIC CONSTANTS

The Water9 documentation refers the user to 40 CFR Part 63 Appendix C for procedures for determination of site-specific biological kinetic constants for use in the Water9 model. A number of continuous-flow and steady-state reactor procedures are given in the appendix, including one for a sealed reactor test, which can be performed in serum bottles, as in the equipment in the Challenge Environmental Systems and other commercially available respirometers. The procedure for calculation of the kinetic coefficients for the Water9 model from batch testing data is detailed in Section III.D.2 and Form XII of Appendix C, and can be summarized as follows:

1. Add a measured amount of biomass from the treatment plant to the closed reactors
2. Add compound to be evaluated and provide mixing and aeration in a closed system

3. Measure the compound concentration at least six times during the course of the run, including at least one measurement after the concentration has been reduced to below the limit of quantification
4. For the each time interval between consecutive pair of analyzed samples, calculate the removal rate in mg/L-hr, the log-mean substrate concentration (LM S) over the interval, and the ratio of the removal rate to the log-mean substrate concentration.
5. Plot the reciprocal of the ratio calculated in step 4 versus log-mean S.
6. Determine K_{max} = 1/ (slope near the y-intercept * MLVSS * headspace factor), where MLVSS is the mixed liquor volatile suspended solids in g/L and the headspace factor is an adjustment based on the Henry's Law Constant of the compound and the amount of headspace in the apparatus relative to the liquid volume. The headspace factor is unitless, with a value slightly less than one for most compounds and respirometers.
7. Determine effective K_1 = (ratio of removal rate/log-mean S)/(MLVSS * headspace factor), with the removal rate being the rate during the time interval in which the substrate concentration was closest to the expected concentration in the full-scale aeration tank.

DETERMINATION OF WATER9 CONSTANTS FROM RESPIROMETRY DATA AND MODELING

The respirometry data and Monod modeling were used to develop COD and styrene profiles giving the decrease in COD and styrene with time, as shown in Figure 4. The styrene profile was then used as a substitute for the sampling and analytical determination of styrene concentration in the Form XII procedure. Data from the respirometry run and calculated Form XII parameters are shown in Table 3.

Table 3. Form XII Data and Calculations

S, mg/L	Time, hr	Rate, mg/L-hr	Log-mean S, mg/L	Ratio of Rate/ LM S, hr^{-1}	Reciprocal Rate, hr
90.60	0.0				
89.95	2.0	0.325	90.27	0.0036	277.7
88.74	4.0	0.604	89.34	0.0068	147.9
79.05	9.0	1.939	83.80	0.0231	43.23
68.52	11.0	5.267	73.66	0.0715	13.99
60.27	12.0	8.246	64.30	0.1282	7.798
49.11	13.0	11.159	54.50	0.2048	4.884
42.16	13.50	13.895	45.55	0.3051	3.278
34.15	14.00	16.022	38.02	0.4214	2.373
25.00	14.50	18.301	29.34	0.6238	1.603
14.78	15.00	20.440	19.45	1.051	0.9514
9.43	15.25	21.402	11.91	1.798	0.5563
4.23	15.50	20.788	6.49	3.203	0.3122
0.03	15.75	16.808	0.860	19.48	0.0513
0.00	16.00	0.1299			

The plot of the reciprocal rate versus the log-mean S is shown in Figures 5 and 6, with Figure 6 showing only the part of the plot near the y-intercept and the linear regression equation, which shows the slope near the intercept.

Figure 5. Plot of Reciprocal rate versus Log-Mean S

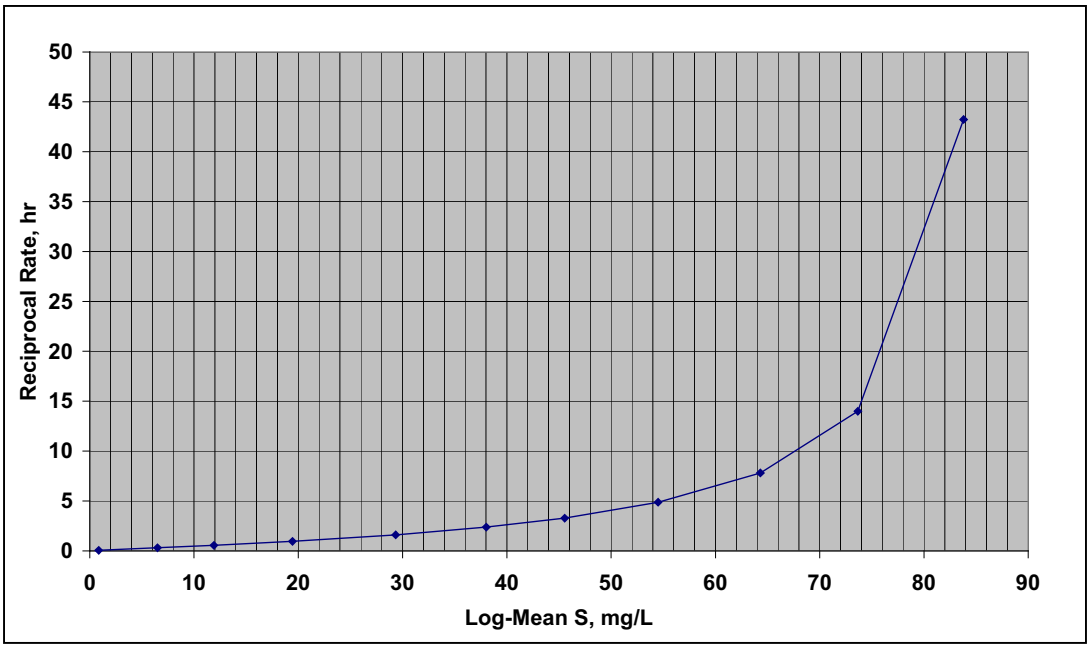
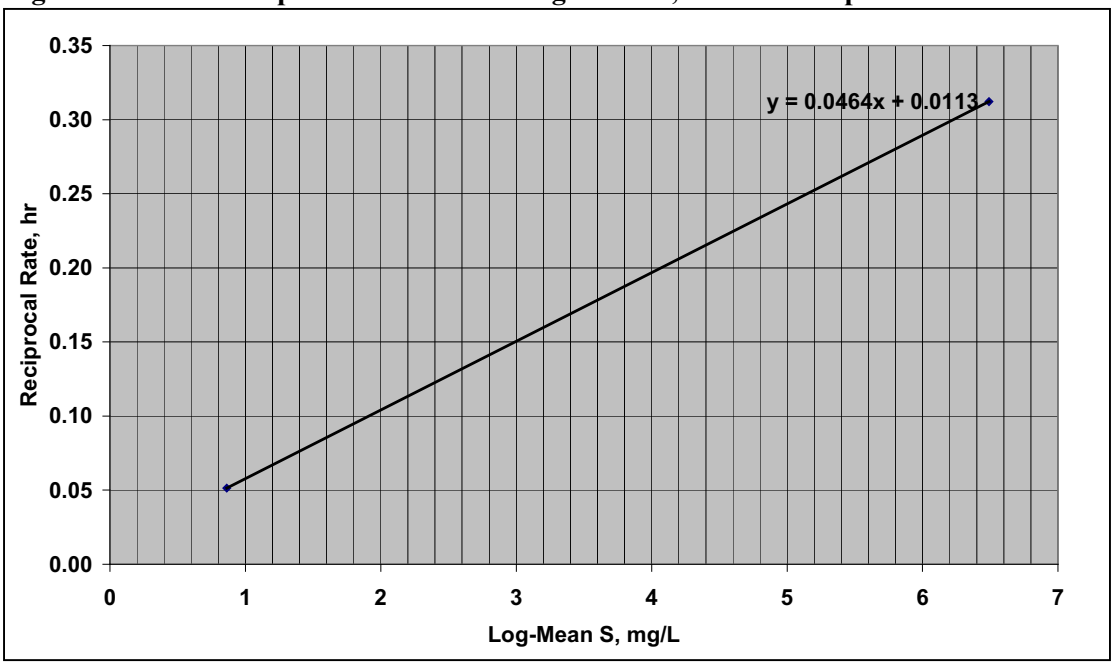


Figure 6. Plot of Reciprocal Rate versus Log-Mean S, Near Intercept



For the data shown in Table 3, the slope in the interval between 15.5 and 15.75 hours was used, which was 0.0464, as shown in Figure 6. This was used to calculate K_{max} from the

slope, the MLVSS as calculated from the kinetic model at 15.5 hours and the headspace factor of 0.968:

$$K_{max} = \frac{1}{\text{slope} * \text{MLVSS} * \text{headspace factor}}$$

$$K_{max} = \frac{1}{\frac{0.0464}{(\text{hr})\text{mg styrene/L}} * \frac{3.02\text{g MLVSS}}{\text{L}} * 0.968} = 7.37 \text{ mg styrene/g MLVSS - hr}$$

The effective K_1 was determined based on the ratio of removal rate to log-mean S for this interval, for which the expected substrate concentration was closest to the expect full scale concentration:

$$K_1 = \frac{\text{ratio of rate/log - mean S}}{\text{MLVSS} * \text{headspace factor}}$$

$$K_1 = \frac{19.48/\text{hr}}{3.02\text{g MLVSS/L} * 0.968} = 6.66 \text{ L/g MLVSS - hr}$$

Table 4 below compares the Water9 constants as determined for the system to the default values and shows the estimated emissions and effluent concentrations for styrene in the Bristol WWTP.

Table 4. Kinetic constants, Emissions and Effluent Concentrations

	Water9 Default Ks	Ks from Respirometry
K_{max}, hr-1	31.1	7.37
K_1, L/gm-hr	0.11	6.66
Emissions, g/s	0.2	0.007
Effluent, mg/L	1.2	0.006

The calculation of the slope of the plot of reciprocal rate versus log-mean S and point at which the effective K_1 are selected are highly sensitive to the interval chosen and the closeness of the interval to the y-axis. Use of the respirometry data allows the slope to be determined for a smaller interval than would be typical using discrete-sample substrate monitoring and the interval can be chosen close to the y-axis, which may be difficult to achieve with discrete sample monitoring. In addition, MLVSS may increase over the course of a respirometer run. The Monod model can be used to estimate the MLVSS at the time that corresponds to the rates used to calculate K_{max} and K_1 in the Form XII procedure. These factors may make the coefficients obtained by respirometry more representative of actual biodegradation than coefficients determined from discrete sampling.

REGULATORY CONSIDERATIONS

The purpose of 40 CFR Part 63 Appendix C is to define procedures for calculation of site-specific fraction of organic compounds degraded (F_{bio}) in a biological treatment plant for regulatory determinations under certain Part 63 NESHAP standards. The specific procedures in the Part 63 regulations must be followed for determination of F_{bio} for this purpose.

CONCLUSIONS

There are important differences between the intrinsic Monod biological kinetic constants and the constants used by the Warter9 model. Data obtained from fitting respirometry data to a Monod model can be used to generate a substrate removal profile, which can then be used to determine kinetic constants for the Water9 model in a modification of batch closed-reactor procedure for generating site-specific kinetic constants for the Water9 model.

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