

# **CALIBRATION OF BIODEGRADATION RATE COEFFICIENTS FOR HAZARDOUS AIR POLLUTANTS IN AN INDUSTRIAL ROUGHING FILTER**

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## **ABSTRACT**

Roughing trickling filters are used to reduce organic loadings ahead of the activated sludge process at a Merck & Co. Inc. manufacturing site. The site is subject to the Pharmaceutical MACT (Maximum Achievable Control Technology) Rule, and must demonstrate required reductions of hazardous air pollutants (HAPs). TOXCHEM+ predictive fate software is used at the site to estimate the reduction and removal of the HAPs during wastewater treatment. Site-specific biodegradation rates of the HAPs can be demonstrated as part of an overall strategy to devise the best approach for achieving compliance with the MACT Rule. An experimental sampling program of filter influent and effluent and exhaust air was completed over 2 days to assess the fate of the HAPs in the process, and to estimate site-specific biodegradation rate coefficients for the HAPs for use in the fate modeling software.

In each of 6 tests, mass balances for the organic compounds were constructed around the trickling filter. The difference between calculated mass inputs and outputs was considered to be the mass of compound removed by biodegradation. Following tabulation of the removal of the compounds by the principal fate mechanisms of stripping, effluent pass-through and biodegradation, biodegradation rate coefficients were estimated using TOXCHEM+ for each test. The estimated biorate coefficients were compared to those used in the software database. The biorate coefficients of certain of the compounds were very similar in magnitude to the model defaults (ethanol, acetonitrile, methyl ethyl ketone, hexane), while methanol was substantially lower, and toluene, triethylamine and i-propanol generally higher. The redox environment of the trickling filter may be one reason why some estimated biorate coefficients deviate from the default aerobic biorate coefficient in the software database.

Using TOXCHEM+, the emission rates from the wastewater facility using only a single default biodegradation rate for each compound, and using two biodegradation rate coefficients (calibrated coefficient for the roughing filter, model default coefficient for the activated sludge unit) were compared. The results showed that estimated emission rates were substantially lower (e.g. 73 kg/d (161 lb/d)) using the dual biodegradation rate coefficient model, mostly due to reduced emissions of toluene. The model also showed that the majority of the compound load was removed by the trickling filters, before the activated sludge tanks had any opportunity for removal. The study indicated that model accuracy can be improved by calibration of biodegradation rates for HAPs and VOCs, and in using the dual biodegradation rate coefficient model for estimating emissions. Greater accuracy of emissions predictions makes the model a

better tool for wastewater treatment facility emission evaluations and for decision-making in response to the Pharmaceutical MACT regulations.

## **KEY WORDS**

Trickling filter, Emissions, HAPs, Pharmaceutical, Model

## **BACKGROUND**

A sampling program, consisting of six tests over two days, was conducted at the roughing trickling filters of a Merck & Co. Inc. manufacturing site to estimate biodegradation rate coefficients of target organic compounds. This evaluation would determine if different biodegradation rate coefficients for each compound could significantly improve modeled emission rates, and hence help to determine the preferred approach to achieving compliance of hazardous air pollutant (HAP) removals required by the Pharmaceutical MACT (Maximum Achievable Control Technology) Rule (U.S. EPA, 1998). Under the MACT rule, a site can choose either to demonstrate overall reduction/removal of combined soluble and partially soluble HAPs by 95 % or higher, or to demonstrate reduction/removal of total partially soluble HAPs by 99 % or higher, plus reduction/removal of total soluble HAPs by 90 % or higher.

At Merck's manufacturing sites, the predictive fate software TOXCHEM+ has been used to estimate the fate of HAPs and volatile organic compounds (VOCs) in the wastewater treatment systems. In the software, each contaminant has an assigned biodegradation rate coefficient used in all biological treatment units. The treatment system at the test site uses a roughing trickling filter to reduce the organic loading to the activated sludge treatment system. The biodegradation rate coefficients for many of the organic compounds in TOXCHEM+ are based on suspended growth systems. Because of the different system characteristics (fixed film vs. suspended growth, different organic loading regime), however, a single biodegradation rate coefficient may not be applicable to both systems. Variations in biodegradation rate coefficients due to suspended or fixed growth matrices could have a potentially significant effect on the modeled emission rates of the organic compounds, and hence influence the preferred approach to achieving compliance of HAP/VOC reductions. For this reason, Merck & Co. initiated a sampling program to calibrate the biodegradation rate coefficients for the trickling filters for use in the site wastewater treatment model.

The primary objective of the study was to estimate the biodegradation rate coefficients of HAPs for use in the trickling filter process of TOXCHEM+. The testing approach involved the determination of the actual removal/reduction efficiency of the combined soluble and partially soluble HAPs across the filters during full operation. Influent and effluent liquid samples, and exhaust air vented from the trickling filter were collected for HAP analysis in each test. The analytical data were then used to calibrate the model by adjusting the biodegradation rate coefficient to match the observed removals and fate of the organic compounds. The compounds included for calibration in the study are summarized in Table 1.

The exhaust air was also analyzed for oxygen and carbon dioxide content, permitting estimation of the oxygen mass transfer coefficient " $\alpha K_L$ " for the trickling filter. In addition, hydraulic

tracer studies were conducted after the test to define the retention time of the wastewater in the filter under the test loading conditions. The hydraulic and oxygen mass transfer characteristics are used in TOXCHEM+ for estimating the relative contribution of fate mechanisms (stripping, biodegradation and sorption) to organic contaminant removal. Determination of the parameter values at the site assists in calibration of the trickling filter model. The results of the oxygen mass transfer and hydraulic tracer tests were reported previously (Monteith et al., 2001).

**Table 1 - Contaminants Monitored in Trickling Filter Calibration Study**

Compound	Henry's law Coefficient $L_{liq}/L_{gas}$	Typical Infl. Con'n. mg/L	Trick. Filter Infl. Mass Kg/d (lb/d)
Toluene	2.63E-01	47.00	113 (248)
n-hexane	3.14E+01	16.50	34.5 (76.0)
Acetonitrile	8.16E-04	54.00	146 (322)
Triethylamine	5.00E-03	13.00	33.2 (73.1)
Ethyl ketone	1.04E-04	18.00	48.4 (107)
Ethanol	2.57E-04	294.00	806 (1780)
Dichloromethane	1.21E-01	0.22	0.5 (1.2)
Methanol	2.13E-04	318.00	872 (1920)
Isopropanol	6.14E-04	75.00	204 (449)
Tetrahydrofuran	1.96E-03	7.00	18.8 (41.4)
Acetone	1.50E-03	7.00	18.8 (41.5)
Methyl acetate	4.43E-03	0.02	0.05 (0.1)
Dimethyl formamide	7.77E-06	1.00	2.8 (6.1)

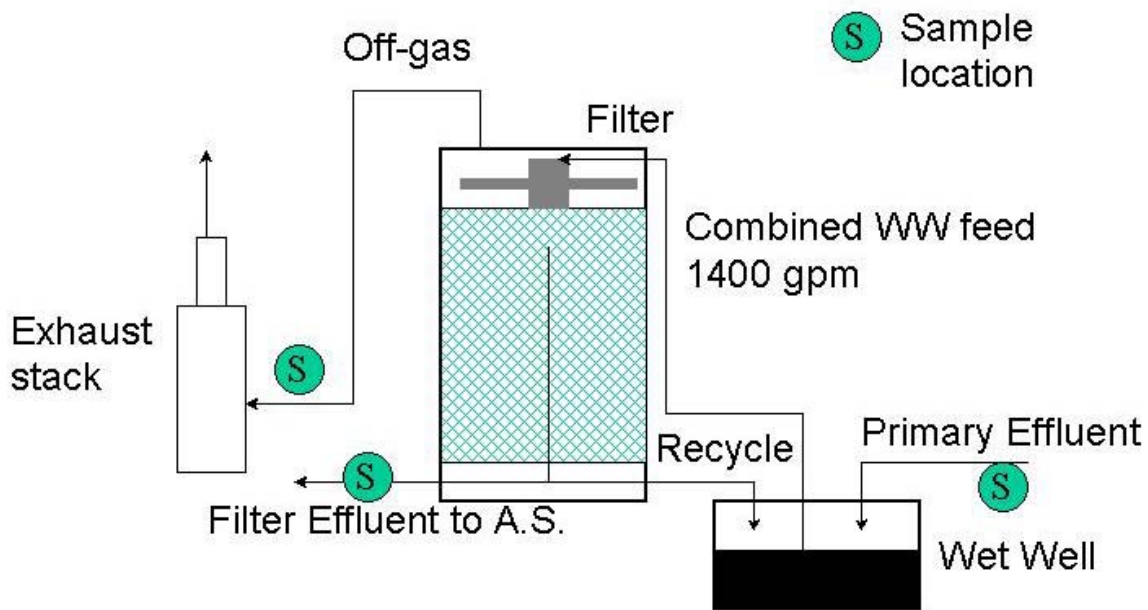
\* shaded compounds are HAPs regulated by the MACT rule

This paper summarizes the calibrating of the site-specific biodegradation rate coefficients of target HAPs and VOCs, and subsequent modeling for estimation of emissions from the roughing trickling filters.

## DESCRIPTION OF TRICKLING FILTERS

The wastewater treatment process includes two roughing trickling filters operated in parallel. Primary effluent is pumped to a stilling well before the filters, where it is combined with recycled trickling filter effluent prior to application to the filter surface. The trickling filters are circular, of 15.2 m (50 ft) diameter, each with a footprint surface area of 182 m<sup>2</sup> (1964 ft<sup>2</sup>), and a media depth in the filter of 6.55 m (21.5 ft). The specific surface area of the media is reported by the manufacturer as 88.5 m<sup>2</sup>/m<sup>3</sup> (27 ft<sup>2</sup>/ft<sup>3</sup>), resulting in a total potential area for transfer of 105,900 m<sup>2</sup> (1,140,000 ft<sup>2</sup>) for each unit. The filters are covered and force-ventilated with ambient air at a rate of 2.36 m<sup>3</sup>/s (5,000 cfm) each to maintain aerobic conditions within the core of the filter media. The exhaust air is discharged to the atmosphere. Trickling filter effluent flows by gravity to the activated sludge process. A schematic diagram of the trickling filter tested, with sampling locations, is depicted in Figure 1.

**Figure 1 - Schematic of Trickling Filter with Sampling Locations**



Each trickling filter operates on a fixed total flow basis of  $0.088\text{m}^3/\text{s}$  (1400 gpm), in which the proportions of feed to recycle flow can be varied. The hydraulic loading rate of the filter on a total flow basis is  $0.000483\text{ m}^3/\text{m}^2\text{-s}$  ( $0.71\text{ gal}/\text{ft}^2\text{-min}$ ), which is slightly below the range of  $0.000543 - 0.00217\text{ m}^3/\text{m}^2\text{-s}$  ( $0.8 - 3.2\text{ gal}/\text{ft}^2\text{-min}$ ) recommended for plastic media roughing filters (Metcalf and Eddy, 1991). The plant has opted to use only one of two pumps for filter loading. The applied loading of  $\text{BOD}_5$  is approximately  $4.65\text{ kg}/\text{m}^3\text{-d}$  ( $290\text{lb}/1000\text{ ft}^3\text{-d}$ ), falling within the design range of  $1.6 - 8.0\text{ kg}/\text{m}^3\text{-d}$  ( $100\text{ to }500\text{ lb}/1000\text{ ft}^3\text{-d}$ ) (Metcalf and Eddy, 1991).

## **SAMPLING PROCEDURES**

**Wastewater.** In these tests, only one of the two parallel filters was tested. The trickling filter influent wastewater samples were collected from the influent wet well of the filter tested. The effluent wastewater samples were collected in the effluent trough before the flow drops into the effluent wet well, to minimize volatilization losses. Grab samples of trickling filter combined wastewater feed, and effluent, were collected once/hour for 12 hours on each of the two sampling days.

The wastewater grab samples were collected at one-hour intervals during each sampling event. The wastewater sampling began 3 hours before collection of the first vent gas sample of the day and continued for 3 hours after the last vent gas sample of the day was collected. Grab samples for VOC analysis were collected in 40 millilitre (mL) clear glass vials with Teflon™-lined septum caps (VOA vials). Sample containers for other wastewater analytes were as specified in 40 CFR 136, Table II. VOC water samples were immediately preserved with HCl to pH 2 and

stored at 4 °C. The maximum holding time for VOC samples was 14 days. Preservation and holding times for the other analytes were as specified in Table II of 40 CFR 136.

**Vent gas.** Trickling filter vent gas samples were collected from the vent duct 3 times on each of the sampling days, and gas flow measurements were conducted before and after each sampling event. Each vent gas sample was collected over a one-hour period at 1000-1100, 1200-1300, and 1400-1500 hours, each day. The vent gas flow rate in the duct was determined by conducting velocity traverses using a pitot tube according to EPA Method 2 of 40 CFR Part 60, Appendix A. The two calculated flowrates (before and after the sampling event) were averaged to get a value representative of the sampling event. The vent gas sample port and the ports for the velocity traverses met the requirements of Method 1 of 40 CFR Part 60, Appendix A with respect to the length of straight pipe (number of pipe diameters) upstream and downstream of the measurement point.

## ANALYTICAL METHODS

**Wastewater.** The grab samples of trickling filter influent and effluent were analyzed individually for the target VOCs. The VOCs were analyzed using EPA Methods 624 and 1671, for the partially soluble and soluble analytes listed in Table 1. The Method 624 list of analytes does not include all of the partially soluble target analytes shown in Table 1. For partially soluble analytes not listed for Method 624, calibration standards and matrix spikes were prepared and tested to demonstrate that the method performance requirements (precision, recovery) of EPA Method 1666 could be achieved for these analytes using Method 624.

The quality assurance/quality control (QA/QC) requirements of each analytical method were followed. In addition, study-specific QA/QC procedures were performed as discussed later in this section.

**Vent gas.** EPA Method 18 of 40 CFR Part 60, Appendix A was used to collect and analyze the grab samples from the trickling filter vent duct. Gas chromatography-mass spectrometry (GC/MS) was used for analysis of the off-gas samples.

## ESTIMATION OF BIODEGRADATION RATE TARGET COMPOUND RATE COEFFICIENTS

Mass balances around the trickling filter were calculated for each test run to estimate the fraction of each of the target organics destroyed by biodegradation in the trickling filter. The general mass balance for any organic compound was of the form:

$$Mass_{in} = Mass_{eff} + Mass_{air} + Mass_{biod} \quad (1)$$

Mass balances were computed using available flow and concentration data. Contaminant masses discharged in the filter effluent and removed by stripping were calculated directly from analytical data. The contribution of biodegradation to removal was estimated as the difference between the influent mass and the sum of the masses in the effluent and off-gas.

The total hydraulic flow applied to the trickling filter was 0.088 m<sup>3</sup>/s (1400 gpm) on both days of testing. The total applied flow ( $Q_{ww}$ ) consisted of the primary clarified wastewater, which varied with time, with the balance comprised of the recycled filter effluent component. Concentrations of the organic compounds were measured in both the primary treated wastewater and trickling filter effluent, and in the filter off-gas. Concentrations of contaminants in the combined wastewater feed were determined by mass balance based on the flows and concentrations of the primary clarifier and recycle streams.

The ventilation rate of the trickling filter was nominally 2.36 m<sup>3</sup>/s (5,000 cfm). Measurements of the ventilation rate and temperature of the vent gas were measured on each of the six sampling campaigns over the two-day study period.

The fraction of each compound removed by biodegradation, referred to as  $f_{bio}$ , was calculated by dividing the mass biodegraded by the influent mass to the filter. Equation (1) can be rearranged in mathematical terms as:

$$f_{biod,i} = \frac{Q_{ww}(C_{ww,i} - C_{eff,i}) - Q_g C_{g,i}}{Q_{ww} C_{ww,i}} \quad (2)$$

where:

$f_{biod,i}$  = fraction of organic compound i biodegraded

$Q_{ww}$  = combined wastewater flow to trickling filter

$Q_g$  = filter ventilation rate

$C_{ww,i}$  = concentration of organic compound i in combined wastewater to trickling filter

$C_{eff,i}$  = concentration of organic compound i in trickling filter effluent

$C_{g,i}$  = concentration of organic compound i in trickling filter vent gas

A trickling filter process alone was created in the TOXCHEM+ model and characterized with the appropriate parameters for each test campaign. The biodegradation rate coefficient  $k_b$ , either alone or together with the solid/liquid partition coefficient  $K_p$ , was adjusted by iteration until the  $f_{bio}$ , the fraction stripped and fraction pass-through terms calculated by the model coincided as closely as possible to the corresponding terms calculated from the field measurements. At the point of closest agreement between modeled and measured  $f_{bio}$  and fractions stripped and in effluent pass-through, the values of  $k_b$ , and  $K_p$  if varied, were saved as unique compound properties in the model user chemical database. These user chemical compounds would then be used in the TOXCHEM+ model as the trickling filter biorate (and sorption) coefficients, distinct from the values for the parameters in the default database used with the suspended growth activated sludge systems. The procedure was completed in each test run for each compound with measurable liquid (influent and effluent) and gas phase concentrations.

## RESULTS

**Model Biorate Calibration.** The results of the software iterations in the six test runs to match measured and predicted compound fates are summarized in Tables 2 and 3 for tests on Days 1 and 2, respectively. The derived modeling parameters  $k_b$  (first order biodegradation rate

coefficient) and  $K_p$  (solids sorption coefficient), resulting from matching the measured and predicted fate mechanisms, are presented in Table 4.

**Table 2 - Comparison of Measured and Predicted Compound Fate Mechanisms in Trickling Filter, Day 1**

Compound	Time	Measured Fate (% of Influent)			Calibrated Model Fate (% of Influent)		
		Stripped	Effluent	Biodegr.	Stripped	Effluent	Biodegr.
Acetonitrile	1100	4.70	18.98	76.32	3.90	19.76	76.34
	1300	4.19	24.55	71.26	5.17	23.58	71.25
	1500	4.74	36.00	59.26	4.66	36.04	59.30
2-Butanone	1100	9.46	23.81	66.73	9.49	23.59	66.91
	1300	4.64	22.50	72.85	4.11	22.90	72.99
	1500	13.47	33.64	52.89	13.80	33.41	52.79
Ethanol	1100	0.11	<6.54*	>93.36	0.68	5.22	94.10
	1300	0.17	<8.13	>91.70	0.76	4.29	94.95
	1500	0.12	<9.09	>90.79	0.92	2.52	95.56
Hexane	1100						
	1300	79.39	9.80	10.81	79.02	10.53	10.45
	1500						
Methanol	1100	0.79	12.15	87.06	0.73	12.27	87.01
	1300	0.59	14.03	85.38	0.91	14.02	85.07
	1500	0.75	19.84	79.41	0.98	19.92	79.10
2-Propanol	1100	1.03	<17.01	>81.97	1.36	16.03	82.62
	1300	0.71	<18.55	>80.74	0.83	11.91	87.26
	1500	0.77	<20.92	>78.31	0.77	7.36	91.87
Toluene	1100	48.50	7.03	44.47	48.52	7.05	44.42
	1300	36.97	7.43	55.60	39.93	7.81	52.25
	1500	44.39	10.28	45.32	46.60	9.64	43.76
Triethylamine	1100	<0.95	81.25	>17.80	4.39	77.83	17.78
	1300	<0.17	10.55	>89.28	4.86	10.55	84.60
	1500	<0.08	15.36	>84.56	6.32	15.56	78.12

\* values noted by the symbol < or > are based on liquid concentrations less than the method detection limit

In most cases, adjustment of  $k_b$  (biodegradation rate coefficient) and  $K_p$  (sorption coefficient) was able to match closely the removal efficiencies predicted by the model with those determined from the field data. The greatest difficulty in matching field and predicted removal efficiencies occurred with triethylamine. The observed field and predicted stripping efficiencies could not be closely matched without allowing the value of Henry's law coefficient in the database to vary.

**Table 3 - Comparison of Measured and Predicted Compound Fate Mechanisms in Tricking Filter, Day 2**

Compound	Time	Measured Fate (% of Influent)			Calibrated Model Fate (% of Influent)		
		Stripped	Effluent	Biodegr.	Stripped	Effluent	Biodegr.
Ethanol	1100	0.21	<4.27*	>95.92	0.67	4.36	94.97
	1300	0.19	<3.50	>96.31	0.61	3.18	96.21
	1500	0.17	<4.42	>95.40	0.55	1.97	97.48
Methanol	1100	0.58	7.50	91.92	0.65	7.72	91.93
	1300	0.47	21.22	78.31	0.73	20.50	78.76
	1500	0.57	34.78	64.65	0.82	34.31	64.87
2-Propanol	1100						
	1300	0.73	16.61	82.66	0.94	16.38	82.69
	1500						
Toluene	1100	70.5	17.6	11.9	70.5	17.9	11.7
	1300	56.1	13.3	30.6	56.21	13.28	30.51
	1500	65.3	17.6	17.1	65.1	17.8	17.1

\* values noted by the symbol < or > are based on liquid concentrations less than the method detection limit

Because the modeling exercise assumed that Henry's law coefficient was a well-established parameter with less uncertainty associated with it than either  $k_b$  or  $K_p$ , the default value of  $H_c$  from the model database was not allowed to vary. The values of  $H_c$  used in the TOXCHEM+ database are from Appendix C to Part 63 of 40 CFR, (known as the HON Rule). Modeling efforts suggested that the measured triethylamine field data could only be matched with model simulations when the value of  $H_c$  was reduced to  $0.0005 L_{liq}/L_{gas}$ , an order of magnitude lower than the value currently in the database. With a reduced Henry's law coefficient of approximately 0.0005, a biodegradation rate coefficient of 0.0004 L/mg VSS-h and  $K_p$  value of 0.001 L/g VSS would more closely match the measured removal efficiencies.

The inability of the model to track the measured fate of triethylamine would appear to result from the pH-dependent equilibrium of the compound between ionized (non-strippable) and un-ionized (strippable) forms. Zabik (1999) notes that up to a pH of 9 in wastewater, only 1.9 % of triethylamine is available for stripping, and it is only above a pH of 10 that any significant stripping occurs. Because the trickling filter is a biological system, which would typically operate in the pH range of 6.5 to 8, only a very small fraction of triethylamine would be available for stripping. For the model to predict the stripping accurately, a correction factor for the un-ionized fraction would need to be applied to the value of  $H_c$  in the TOXCHEM+ database.



**Table 4 - TOXCHEM+ Model Default and Experimentally Derived Compound Database Parameters for Tricking Filter**

Day	Time	Parameter*	Toluene	Methanol	Ethanol	I-Propanol	Acetonitrile	Triethylamine	Methyl Ethyl Ketone	Hexane
Default	--	K <sub>p</sub>	0.592	0.00494	0.00912	0.0148	0.008766	0.09572	0.0195	3.34
	--	k <sub>b</sub>	0.00354	0.0053	0.0009	0.00008	0.0001	0.0011	0.0002	0.0015
1	1100	K <sub>p</sub>	0.72	0.27	0.00912	0.0148	0.015	28	0.81	
		k <sub>b</sub>	0.0112	0.00058	0.0009	0.0004	0.000313	0.0004	0.00033	
	1300	K <sub>p</sub>	0.72	0.27	0.00912	0.8	0.015	1	2.3	1
		k <sub>b</sub>	5	0.000455	0.0009	0.001	0.00022	0.012	0.0013	0.0014
	1500	K <sub>p</sub>	1.1	1.2	0.00912	0.8	2	1.9	1.6	
		k <sub>b</sub>	6	0.00045	0.001	0.0025	0.00022	0.012	0.00019	
2	1100	K <sub>p</sub>	3	0.1	0.2					
		k <sub>b</sub>	0.0019	0.0011	0.0017					
	1300	K <sub>p</sub>	2.1	0.1	0.2	0.8				
		k <sub>b</sub>	0.15	0.00064	0.00235	0.00102				
	1500	K <sub>p</sub>	2.7	0.1	0.2					
		k <sub>b</sub>	0.01	0.00039	0.004					
Arith. Mean		K <sub>p</sub>	1.72	0.34	0.105	0.604	0.677	10.3	1.57	1.0
Geo. Mean			1.46	0.21	0.043	0.295	0.077	3.76	1.44	1.0
Arith. Mean		k <sub>b</sub>	1.86	0.00060	0.0023	0.0012	0.00025	0.0081	0.00061	.0014
Geo. Mean			0.10	0.00056	0.0019	0.0010	0.00025	0.0039	0.00043	.0014

\* Units for K<sub>p</sub> are L/g VSS and for k<sub>b</sub> are L/mg VSS-h

Experimentally derived  $K_p$  values were in almost all cases larger than the model default values, by factors ranging from 1.00 (ethanol, I-propanol) to 293 (triethylamine) (Table 5). The high value for triethylamine is questionable, based on the estimated pass-through fraction for the 1100 hour sample on Day 1.

Estimated biodegradation rate coefficients were determined to range above and below the model default values. Table 5 shows that the biodegradation rate coefficients of certain of the analytes were very similar in magnitude to the model defaults (ethanol, acetonitrile, methyl ethyl ketone, hexane), while methanol was substantially lower, and toluene, triethylamine and i-propanol generally higher.

The reason that methanol is the only compound with a measured biodegradation rate coefficient lower than its corresponding default value in the model database is not entirely clear. The difference may be due to the possibility of different redox environments under which the parameters were determined. The biodegradation rate coefficient in the TOXCHEM+ database was determined by Barton and McKeown (1991), in an aerated basin treating pulp mill wastewater. The methanol coefficient derived from the trickling filter data may have resulted from a reactor that probably had zones of anoxic or anaerobic activity. Although this discussion is applicable to the other compounds, the preference of the microbes for utilizing the different organic compounds in anoxic or anaerobic environments has not been sufficiently documented for inclusion in the model.

Because of the limited number of detectable concentrations of compounds on Day 2, the opportunity to compare biodegradation rate coefficients from the two different loading rates is limited to toluene, methanol and ethanol. A very substantial difference between biodegradation rate coefficients was determined for toluene on the two days, with much less difference between coefficients for methanol and ethanol (Table 6). The difference for toluene may be due to the use of the direct injection analytical technique by the analytical laboratory for toluene on Day 2, as opposed to the GC/MS procedure used for the analysis on Day 1. Differences in the biodegradation rate coefficients were tested for significance by pooling the data for the two days. The difference between means using the t-statistic was not significant for any of the three compounds at the 5 % probability level. Differences between the mean daily rate coefficients were somewhat obscured, however by the limited number of measurements.

Discussion of oxygen transport in trickling filters by Mehta *et al.* (1972), suggests that the removal of organic compounds in the filter may be occurring in a predominantly anaerobic environment. Through detailed mathematical derivations, Mehta *et al.* suggest that a filter must have greater than 5/8 of the saturation concentration of oxygen at a wastewater temperature of 15 °C to maintain aerobic conditions. The temperature of the wastewater treated by the trickling filter was approximately 30 °C, which should have a saturation concentration of oxygen of 7.54 mg/L at one atmosphere (Metcalf & Eddy, 1991). For aerobic reduction of the compounds to occur, the trickling filter effluent should exhibit a dissolved oxygen (D.O.) level of  $0.625 \times 7.54 = 4.71$  mg/L, according to Mehta *et al.* (1972).

**Table 5 - Ratio of Experimentally Derived to Model Default Parameters**

Parameter	Day	Time	Toluene	Methanol	Ethanol	I-Propanol	Acetonitrile	Triethylamine	Methyl Ethyl Ketone	Hexane
K <sub>p</sub> (L/mg VSS-h)	1	1100	1.22	54.7	1.00	1.00	1.71	293	41.5	
		1300	1.22	54.7	1.00	54.1	1.71	10.4	118	0.30
		1500	1.86	243	1.00	54.1	228	19.8	82.1	
	2	1100	5.07	20.2	21.9					
		1300	3.54	20.2	21.9	54.1				
		1500	4.56	20.2	21.9					
k <sub>b</sub> (L/g VSS)	1	1100	3.16	0.109	1.00	5.00	3.13	0.36	1.65	
		1300	1,410	0.085	1.00	12.5	2.2	10.9	6.5	0.93
		1500	1,690	0.084	4.44	31.3	2.2	10.9	0.95	
	2	1100	0.537	0.208	1.89					
		1300	42.4	0.12	2.61	12.75				
		1500	2.82	0.074	4.44					

**Table 6 - Comparison of Estimated Modeling Parameters**

Parameter	Statistic	Toluene	Methanol	Ethanol	I-Propanol	Acetonitrile	Triethylamine	Methyl ethyl ketone	Hexane
k <sub>b</sub> day 1 (L/mg VSS-h)	Arith. Mean	3.67	0.00050	0.001933	0.0013	0.000251	0.00813	0.000607	0.0014
	Std. Dev.	3.21	7.37E-05	0.001796	0.0011	5.37E-05	0.00670	0.000605	
	Geo. Mean	0.695	0.00049	0.00148	0.001	0.000247	0.00386	0.000434	0.0014
k <sub>b</sub> day 2 (L/mg VSS-h)	Arith. Mean	0.054	0.00071	0.00268	0.0012				
	Std. Dev.	0.083	0.00036	0.00119					
	Geo. Mean	0.014	0.00065	0.00252	0.0012				
K <sub>p</sub> day1 (L/g VSS)	Arith. Mean	0.847	0.58	0.00912	0.538	0.677	10.3	1.57	1
	Std. Dev.	0.219	0.54	0	0.453	1.15	15.3	0.745	
	Geo. Mean	0.829	0.44	0.00912	0.212	0.0766	3.76	1.44	1
K <sub>p</sub> day 2 (L/g VSS)	Arith. Mean	2.60	0.1	0.2	0.8				
	Std. Dev.	0.458	0	0					
	Geo. Mean	2.57	0.1	0.2	0.8				

Table 7 lists the D.O. levels in the wastewater feed and trickling filter effluent during the two days of testing. Clearly, the raw wastewater feed is well below the D.O. level that should be found in the effluent for aerobic degradation to occur. In fact, the trickling filter serves as an aeration device, increasing the D.O. level by approximately 1 to 1.5 mg/L.

**Table 7 - Trickling Filter Influent and Effluent Dissolved Oxygen Levels**

Day	Time	Influent		Effluent	
		D.O. (mg/L)	Temp. (°C)	D.O. (mg/L)	Temp. (°C)
1	10-11	0.15	30.4	2.05	30.7
	12-13	0.10	31.2	1.35	31.1
	14-15	0.13	32.1	1.4	31.9
	Overall	0.13	31.5	1.52	31.4
2	10-11	0.83	31.6	2	31.9
	12-13	2.5	29.5	2.6	31.2
	14-15	2.35	28.9	3.25	30.1
	Overall	1.64	30.1	2.74	30.7

The redox environment of the trickling filter may be one reason why the estimated biodegradation rate coefficient for methanol is less than the default aerobic biodegradation rate coefficient in the TOXCHEM+ database. Organic compounds may be utilized at a different rate in aerobic and anaerobic environments. This may explain why there is no apparent difference between rate coefficients, as measured in this study and in the model database, for a compound such as ethanol, but methanol is consumed at a lower rate in the filter than the data base would suggest.

A comparison of emissions from the treatment facility, using the TOXCHEM+ model with both the single rate coefficient, and the dual rate coefficients, is presented in Table 8 using the test conditions of Day 1 at 1300 hours. This example shows that for toluene, use of the dual biodegradation rate coefficients results in significantly lower emissions from the wastewater treatment facility. Almost all emissions result from the trickling filters, with minor contributions from the activated sludge unit and other downstream processes.

The efforts of calibrating the model with a second biorate coefficient are clearly beneficial for the estimation of emissions from the treatment facility. For example, the simulations for the operating conditions during the test at 1300 hours on Day 1 show a reduction of 73 kg/d (161 lb/d) of total VOCs and HAPs, most of which is contributed by toluene. While calibration of the biodegradation rate coefficients may result in minor reductions in emission rate for most target HAPs, or even an increase in emissions (e.g., methanol), the potential emission rate reduction, as observed with toluene alone can make the effort valuable. The study indicates that use of more than one aerobic biodegradation

rate coefficient in predictive fate software can improve the accuracy of secondary emission estimates.

**Table 8 - Comparison of Wastewater Treatment Facility Emissions with Single and Dual Biodegradation Rate Coefficients (data from Day 1, 1300 hours)**

Compound	Total Mass Emission, kg/d (lb/d)			
	Single Default Rate Coefficient	Dual Rate Coefficients		
		Default (AS)	User (TF)	Total
Acetonitrile	38.8 (85.5)	0.79 (1.75)	31.2 (68.9)	32.0 (70.6)
2-Butanone	7.1 (15.7)	0.13 (0.28)	2.15 (4.73)	2.27 (5.01)
Ethanol	14.9 (32.8)	0.02 (0.05)	14.9 (32.8)	14.9 (32.8)
Hexane	2.16 (4.77)	0.28 (0.61)	1.58 (3.49)	1.86 (4.10)
Methanol	23.0 (50.8)	0.01 (0.02)	27.0 (59.4)	27.0 (59.5)
2-propanol	11.5 (25.3)	0.44 (0.96)	7.09 (15.6)	7.52 (16.7)
Toluene	169 (373)	0.49 (1.08)	115 (254)	116 (255)
Triethylamine	14.1 (31.1)	0.03 (0.07)	6.57 (14.5)	6.60 (14.6)
<b>TOTAL EMISSIONS</b>	281 (619)	2.19 (4.82)	206 (454)	208 (458)

## SUMMARY

A sampling program consisting of six tests was conducted at the trickling filters of the wastewater treatment facility at a Merck & Co. Inc. manufacturing site. Liquid and off-gas samples from the trickling filter were collected and analyzed for volatile organic compounds (VOCs) and hazardous air pollutants (HAPs) for the purpose of estimating biodegradation rate coefficients of the target organic compounds in the trickling filter. Estimation of the rate coefficients is part of Merck & Co.'s strategy to comply with compound removal requirements of the Pharmaceutical MACT regulation.

In each test, mass balances for the organic compounds were constructed around the trickling filter, quantifying masses lost from the filter in liquid effluent and off-gas samples relative to the input mass. The difference between calculated mass inputs and outputs was considered to be the mass of compound removed by biodegradation. The removal of the compounds by the principal fate mechanisms of stripping, effluent pass-through and biodegradation were tabulated. Biodegradation rate coefficients and solids sorption parameters for each test were then estimated using the TOXCHEM+ predictive fate software.

Estimated biodegradation rate coefficients ranged above and below the model default values in the TOXCHEM+ database. The rate coefficients of certain of the compounds were similar in magnitude to the model defaults (ethanol, acetonitrile, methyl ethyl ketone, hexane), while the rate coefficient for methanol was substantially lower, and those for toluene, triethylamine and i-propanol were generally higher.

Measured dissolved oxygen (D.O.) levels in the primary clarifier effluent discharged to the trickling filter and in the filter effluent revealed the filter acted as an aeration device. Discussion of oxygen transfer in trickling filters in the technical literature suggested that the removal of organic compounds in the filter may be occurring in a predominantly anaerobic environment. The redox environment of the trickling filter may be one reason why some estimated biodegradation rate coefficients deviate from the default aerobic biorate coefficient in the TOXCHEM+ database.

The wastewater treatment facility was configured in TOXCHEM+ so that the trickling filter used the newly calibrated biodegradation rate coefficients for the target compounds, while the downstream processes, including activated sludge units, used the model default biorate coefficients. A comparison of the emissions from the wastewater facility, using only a single default biodegradation rate for each compound, and using two biodegradation rates, showed that estimated total emission rates were substantially lower using the dual rate coefficient model. For the comparison based on the test data from Test 2 on Day 1, emissions of the target compounds were lower by 72.8 kg/d (161 lb/d), mostly due to reduction in the toluene emission rate. The model also showed that the majority of the compound load was removed by the trickling filters, before the activated sludge tanks had any opportunity for removal.

The study indicates that model accuracy can be improved by calibration of biodegradation rates for HAPs and VOCs, and in using the dual biodegradation rate coefficient model for estimating emissions. Improved accuracy of emissions predictions makes the model a better tool for wastewater treatment facility emission evaluations and for decision-making in response to the Pharmaceutical MACT regulations.

## REFERENCES

- Barton, D.A. and McKeown, J.J. (1991). Field Verification of Predictive Modeling of Organic Compound Removal by Biological Wastewater Treatment Processes. *Environ. Progress*, **10(2)**, 96.
- Mehta, D.S., Davis, H.H. and Kingsbury, R.P. (1972). Oxygen Theory in Biological Treatment Plant Design. *Journal, Sanitary Engineering Division, ASCE*, **98(SA3)**, 471.
- Metcalf and Eddy, 1991. *Wastewater Engineering: Treatment, Disposal, Reuse*. McGraw-Hill, Toronto.
- Monteith, H., Watts, R. and Tischler, L. (2001). *Hydraulic and Oxygen Transfer Characteristics of an Industrial Roughing Filter*. Paper presented in Session 22, WEFTEC 2001, Atlanta, GA October 14-17.
- U.S. EPA (1998). 40 CFR 63, No. 182. *National Emissions Standards for Hazardous Air Pollutants for Source Categories: Pharmaceuticals Production*, Sept. 21.
- Zabik, S. (1999). Data from presentation to PhRMA workshop, week of Dec. 6/99.