The Use of 40 CFR 63 Appendix C in Determining Fraction Biodegraded (Fbio) in a Biological Treatment Unit

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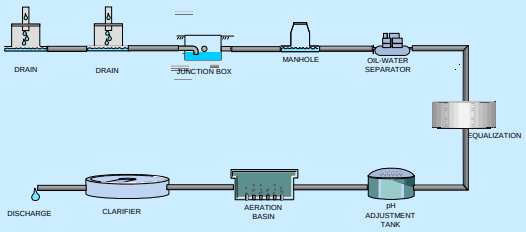
What is Appendix C?

- Located in 40 CFR Part 63 (at the end..)
- Provides procedures for calculating biodegradation of organic compounds in a biological treatment unit.

Industrial Wastewater Treatment



Fr (fraction removed) = Fe (fraction emitted) +Fbio (fraction biodegraded)

Picture courtesy of Minerva De Leon, R6, Houston

Where is Appendix C Used ?

- Used for compliance with MACT and NSPS governing air emissions from industrial wastewater treatment systems
  - HON, MON, Pharmaceuticals, P&R
  - SOCMI NSPS YYY (not final yet)
  - Petroleum Refineries (Subpart CC) Proposed amendments
- Used for developing air emission estimates from industrial wastewater treatment systems
  - Emission inventories
  - Permits

Fe and Fbio Calculations- CSTR System

- $QC_o = QC_L + VKmax(b)C_L/(K_S+C_L) + KVC_L$
- $Fe = KAC_L/QC_o$
  - K= Mass transfer coefficient
  - A= Area
  - C_L = Concentration in the effluent;
  - Q = flow
  - C_o= Initial concentration
- $Fbio = VKmax(b)C_L/[(Ks+C_L)QC_o]$
  - V= Volume of reactor
  - b = biomass
  - Kmax = Monod constant
  - Ks = Half saturation constant

Figure 1 of Appendix C

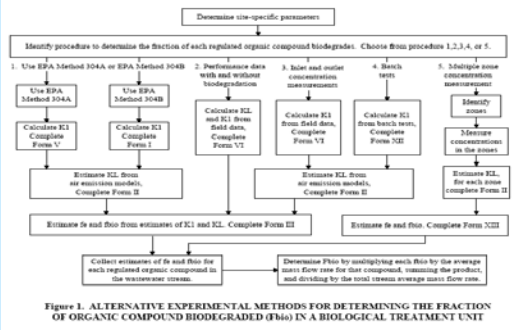


Figure 1. ALTERNATIVE EXPERIMENTAL METHODS FOR DETERMINING THE FRACTION OF ORGANIC COMPOUND BIODEGRADED (Fbio) IN A BIOLOGICAL TREATMENT UNIT

Bioreactor: Determination of Site-Specific Biorate

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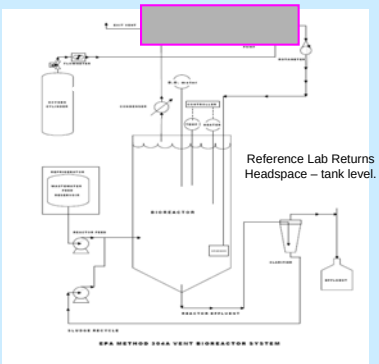
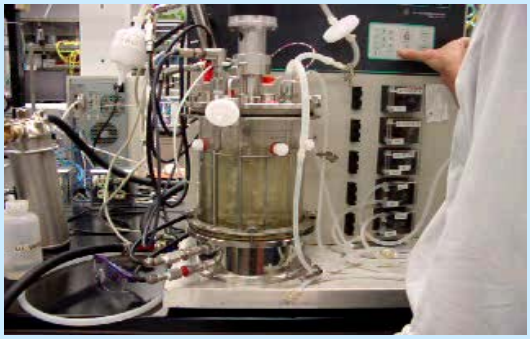


Bioreactor

Bioflow 3000*



Bioreactor

Bioreactor – Controls, Sampling and Measurements

- Inflow-to match RT of full scale unit. Mass flow controller.
- Outflow- Level Control–gravimetric check.
- pH, DO & temperature set & (data logged).
- Exit vent – the real replacement for Henry's Law. Mass Flow Meter.
- Sludge – controlled manually by levels.
- Biomass – VSS representing cell mass. Some accumulation on the sides.
- Physical measurements on bench top unit

Methods

- ✓pH – standard methods and calibration. Data logged.
- ✓DO – standard methods and calibration. Data logged.
- ✓Volatiles – SW-846, 8260, Purge and Trap
- ✓Exit vent – TO-15, average response factor.
- ✓Flow rates NIST (within 2 years) calibrated
- ✓Biology – See protocol slide later.

Physical Controls

- ❖ pH between 7.2 & 7.8 and automatically regulated (tighter than full scale unit)
- ❖DO at 3.0 but for this unit at from 5.0 to 7.0 because recycler/blower not used.
- ❖Temperature at 26^0 C and easiest to control.
- ❖Agitation rate/DO cascaded with agitation set to lower limit.
- ❖All parameters measured more frequently then sample collection.

Biomass (VSS) Measurements

Biomass from TCEQ determinations.			
		VSS	
Work Order	date	mg/l	g/l
0611031-03	22-Nov-06	1160	1.160
0611036-06	24-Nov-06	1080	1.080
0611031-10	25-Nov-06	928	0.928
0611031-14	26-Nov-06	1020	1.020
0611035-02	27-Nov-06	1434	1.434
0611035-05	28-Nov-06	928	0.928
average			1.092
(mg/l)(1g/1000 mg) = g/l			

These were contracted out but other solids determinations, not used in the calculations, were done during sample collection in order to return sludge.

Exit Vent Flow Measurements

exit vent rate SCCM							
N	28-Nov-06	27-Nov-06	27-Nov-06	25-Nov-06	26-Nov-06	average	
1	357	349	371	376	336	358	
2	361	372	349	355	350	357	
3	311	371	326	365	352	345	
4	347	366	317	346	335	342	
5	360	344	311	365	341	344	
6	354	366	294	348	358	344	
7	313	370	331	352	354	344	
8	361	359	316	332	359	345	
9	323	325	319	347	324	328	
10	319	359	327	357	323	337	
11	336	331	334	339	323	333	
12	333	342	297	336	313	324	
13	328	333	329	345	313	330	
14	352	367	309	338	316	336	
15	332	333	321	324	321	326	
16	340	306	322		341	327	
17	333	313	329		341	329	
18	342	348	301		342	333	
19	345	323	317		324	327	
20	310	335	304		319	317	
21	346	325	322			331	
22	330	327	289			315	
23	299	331	296			309	
24	331	346	331			336	
25	292	285	326			301	
average	334.20	341.04	319.52	348.33	334.25	335	ml/min
						333	sccm
						334	
	(scc/m)/(60s/min)(1000000 cc/meter^3)					0.00000557	m^3/s

Volatiles Result

Date	Inlet Concentration		Outlet concentration		Diff	
22-Nov-06	1620		1		1619	
24-Nov-06	1800		1		1799	
25-Nov-06	1830		1		1829	
26-Nov-06	1680		1		1679	
27-Nov-06	1640		1		1639	
28-Nov-06	1540		1		1539	
average	1685	µg/l	1	µg/l	1684	µg/l
%RSD=	6.59					
	g/m^3 =	(µg/l)(g/1,000,000 µg)(1000 l/m^3)				
	1.685	g/m^3	0.001	g/m^3	1.684	g/m^3
note that the MDL was used for the outlet concentration.						

Vent Concentration

25-Nov-06	ppbv	1.01	0611031-09					
26-Nov-06	ppbv	1.31	0611031-13	RSD =	14.42			
27-Nov-06	ppbv	1.37	0611035-06					
28-Nov-06	ppbv	1.09	0611035-07					
		1.195000	average					
	ppbv = 1 liter/10^9 liters							
g/m^3 = (1 liter benzene/10^9 liters sample)(78g/((22.4(299/273))(1000l/m^3)(1liter benzene/10^9 l ppbv)								
	g/m^3=	3.79932E-06						

Biology Measurements

- *P. Putida* commercial strain – no degradation.
- Special sub-strain, F1, obtained from Ga. Tech.
- Growth in TSA. None in MSA.
- Benzene atmosphere provided – carbon source.
- Other compounds - competition/inhibition.

Acknowledgements

Elizabeth Cannon, EPA Toxics Enforcement Section, Dallas

Mark Rodgers, EPA ORD, Cincinnati

Abel Euresti, EPA Region 6 Lab, Houston

Calculations ….

Calculations… Form V-A - input

Form V-A DATA FORM FOR THE CALCULATION OF K1 FROM A COVERED VENTED BIODEGRADATION UNIT. THE VENT CONCENTRATION IS MEASURED.	Line no.		
NAME OF THE FACILITY for site specific biorate determination			Acme
COMPOUND for site specific biorate determination			benzene
BIOMASS (B, g/L) This is the dried solids that are obtained from the mixed liquor suspended solids in the unit.	1		1.0917
VENT RATE of total gas leaving the unit (G, m^3/s)	2		5.57258E-06
TEMPERATURE of the liquid in the unit (deg. C)	3		26^0 C
INLET CONCENTRATION of compound (C_i, g/m^3 or ppmw)	4		1.685
EXIT CONCENTRATION of compound (C_e, g/m^3 or ppmw)	5	<	0.001
VENT CONCENTRATION of compound (C_v, g/m^3)	6		3.79932E-06
AREA OF REACTOR SURFACE (m^2)	7		0.022431757
VOLUME OF REACTOR (m^3)	8		0.00485
FLOW RATE of waste treated in the unit (m^3/s)	9		8.42014E-08

Calculations… Form V-A Output

Form V-A DATA FORM FOR THE CALCULATION OF K1 FROM A COVERED VENTED BIODEGRADATION UNIT. THE VENT CONCENTRATION IS MEASURED.		Line no.		
Calculation of the Estimate of K1				
TOTAL REMOVAL (g/s)	The result of line 4 minus line 5 multiplied by line result of line 9.	10	>	1.41795E-07
[G C_v/C_E] ESTIMATE (m^3/s)	Vent Rate increased by relative exit concentrations.	11	>	2.1172E-08
[K1 B V + G C_v/C_E] ESTIMATE (m^3/s)		12	>	0.000141795
[K1 B V] ESTIMATE (m^3/s)		13	>	0.000141774
Product of B and V		14		0.005294583
K1 ESTIMATE (L/gMLVSS-hr)		15	>	96.39781805
Equivalent KL		16	>	9.43841E-07

Calculations… Form II

NAME OF UNIT for site specific biorate determination			
NAME OF COMPOUND			benzene
Henry's Law constant for the compound (mole fraction in gas *per* mile fraction in water at 25 degrees Celcius.			[see note]
IDENTIFY THE TYPE OFUNIT			(CHECK ONE BOX BELOW)
	Quiescent impoundment	1	
	Surface agitated impoundment	2	
	Surface agitated impoundment with submerged air.	3	
	Unit agitated by submerged aeration gas.	4	
	EPA Method 304A, Covered unit, UNOX system, or batch scale reactor.	5	√
PROCEDURES BASED UPON THE TYPE OF UNIT - KL for the surface is assumed to be zero. Determine equivalent KL based upon air discharge. Use form V for EPA Method 304A or[?] if the vent concentration is not measured. Use Form V-A if the concentration in the vent is measured.			

Calculations… Form III

Form III DATA FORM FOR THE ESTIMATION OF COMPOUND FRACTION BIODEGRADEED AND AIR EMISSIONS			
NAME OF THE FACILITY for site specific biorate determination			Acme
COMPOUND for site specific biorate determination			benzene
	Line no.		
ESTIMATE OF K1 from form V-A line 15.	1	>	96.39781805
BIOMASS (B, g/L) This is the dried solids that are obtained from the mixed liquor suspended solids in the unit.	2		1.091666667
Volume of full scale EBU in m^3.	3		45411.6
Area of the liquid surface of the full scale treatment system	4		3217.795175
Estimate of KL from full scale system	5	>	
FLOW RATE of water in full scale unit	6		0.788395833

Calculations… Form III (con't)

BIORATE (m^3/s) = (line 1)(line2)(line3)/3600	7	>	1327.460345
AIR STRIPPING (m^3/s) = (line 4)(line5)	8	>	0.003037086
EFFLUENT DISCHARGE (m^3/s). Line 6	9		0.788395833
TOTAL OF THE THREE LOSS MECHANISMS. Lines 7 + 8 + 9	10	>	1328.251778
Fraction Biodegraded (Line 7/Line 10)	11		0.999404154
Fraction air emissions. (Line 8/line 10)	12		2.28653E-06
Fraction remaining in unit effluent. (Line 9/line 10)	13	<	0.000593559
Total: Lines 11+12+13 should equal 1.	14		1

System Negative Control

Although there is no specific mention of a negative control on the entire Bioreactor (system blank), a rough approximation was done in the set up. This procedure will be further tested and documented at a later date but in this preliminary trial, there was a sizeable concentration in the exit vent even with all parameters normalized for the main test conditions. When this analysis was done, the system was in the preliminary stages for leak testing and it cannot be considered as a blank for "Acme." It was done utilizing biosolids from"Ajax" and the results assume that there were no viable organism, an assumption that was not tested. This system (Ajax's) had not not been operating for some time and this perceived inactivity of the bioreaction may speak to the possible quick reversion of the organism.

Projected

- Variety of positive & negative systems controls.
- Adjusting for non-zero effluent concentrations.
- Addition of vacuum controller for recirculation.

or

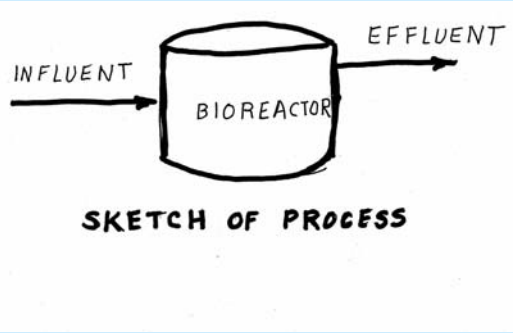
- Use of injected air/O_2 only (to conform with unit changes).
- Use of mobile lab for real time analyses at unit w/hot work permit.

On-site Sampling & Analysis

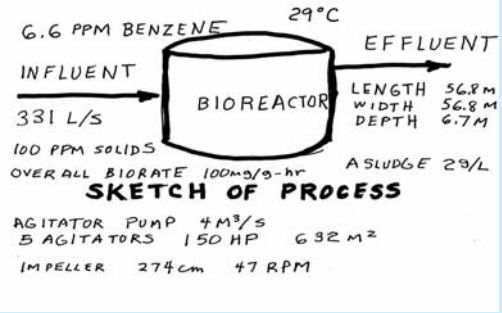
Use of Site Specific Biorate to Model Fbio for a Full Scale System

- Use WATER9 to do the calculations in Appendix C.
  - WATER9 will calculate K_L based on system parameters
  - K_1 from the bioreactor is also an input
  - Consider additional factors for the full scale system with WATER9

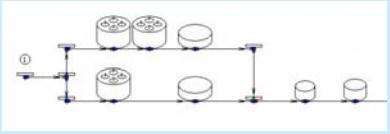
Flow diagram overview sketch



Flow diagram sketch with process information



WATER9 Flow diagram



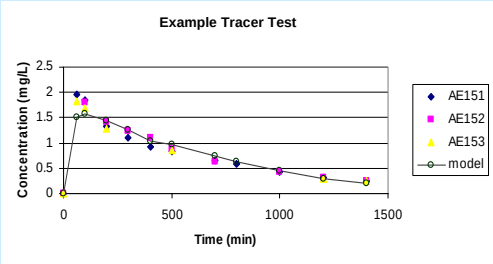
Special Considerations I

- Thoroughly Mixed Units
  - How to tell?
  - How to remodel?
  - What tools are available?
    - http://www.epa.gov/ttn/atw/nsps/socww/socwwpg.html

Special Considerations II

- WATER9 Mixing Analysis
  - Hydraulic residence time is 18 hours
  - Air stripping half life is 14 minutes if quickly mixed
  - Time for both air and biological removal is 11 seconds if quickly mixed
  - Pump mixing time is 90 minutes
- Mixing tests
  - Feed bypassing
  - Tracer testing in full scale reactor

Mixing Tracer Testing



Special QA Procedures

- Laboratory reactor with no biomass
- Laboratory reactor with lower residence time (to enable measurement of reactor concentrations)
- Laboratory reactor with Henry's law constant verification
- Laboratory reactor with higher air purge rate (simulate higher mass transfer).
- Scale-up problems: volatiles rapidly lost in full scale system, no biological adjustment for those.

Further Acknowledgements: Rusty Herbert, Nghia Nguyen & Mel Ritter.

*Bioflow 3000, which is shown and mentioned in this presentation, is a product name for the bench top bioreactor made by New Brunswick Scientific, Edison, N.J.

*No endorsement, either implicit or explicit, is made by the Environmental Protection Agency, or the presenters, as to the usefulness, preference or applicability of any product mentioned in this presentation.

Questions?