6560-50-P

U.S. ENVIRONMENTAL PROTECTION AGENCY

40 CFR Part 63

[OAR-2003-0191; FRL-]

RIN 2060-AE-94

Appendix C to 40 CFR Part 63--Determination of the Fraction Biodegraded (F_{bio}) in a Biological Treatment Unit

AGENCY: Environmental Protection Agency (EPA).

ACTION: Proposed rule; amendments.

SUMMARY: This action proposes amendments to appendix C to 40 CFR part 63. Appendix C defines the procedures for an owner or operator of a facility that generates wastewater to calculate the site-specific fraction of organic compounds biodegraded (F_{bio}) in a biological treatment unit. The proposed amendments to Appendix C would add a non-speciated test procedure to the batch test procedures for use in demonstrating compliance with wastewater rules that regulate volatile organic compounds (VOC), such as the synthetic organic chemical manufacturing industry (SOCMI) Wastewater new source performance standards (NSPS). The proposed amendments would also make minor editorial changes throughout appendix C.

DATES: Comments. Comments must be received on or before

[INSERT THE DATE 60 DAYS AFTER PUBLICATION OF THE PROPOSED RULE IN THE FEDERAL REGISTER].

Public Hearing. If anyone contacts EPA requesting to speak at a public hearing by [INSERT THE DATE 20 DAYS AFTER PUBLICATION OF THE PROPOSED RULE IN THE FEDERAL REGISTER], a public hearing will be held on [INSERT THE DATE 30 DAYS AFTER PUBLICATION OF THE PROPOSED RULE IN THE FEDERAL REGISTER]. Persons interested in presenting oral testimony or inquiring as to whether a hearing is to be held should contact JoLynn Collins, Waste and Chemical Processes Group, Emissions Standards Division (C439–03), U.S. EPA, Research Triangle Park, NC 27711, telephone (919) 541–5671 at least 2 days in advance of the public hearing.

ADDRESSES: Comments. Submit your comments, identified by Docket ID No. OAR-2003-0191, by one of the following methods to the docket. If possible, also send a copy of your comments to Mary Tom Kissell by either mail or e-mail as identified in the FOR FURTHER INFORMATION CONTACT section.

1. Federal eRulemaking Portal: http://www.regulations.gov. Follow the on-line instructions for submitting comments.

2. Agency Website: http://www.epa.gov/edocket. EDOCKET, EPA's electronic public docket and comment system, is EPA's preferred method for receiving comments. Follow the on-line instructions for submitting comments.
3. Mail: Air Docket, Environmental Protection Agency, Mailcode: 6102T, 1200 Pennsylvania Ave., NW., Washington, DC 20460. In addition, please mail a copy of your comments on the information collection provisions to the Office of Information and Regulatory Affairs, Office of Management and Budget (OMB), Attn: Desk Officer for EPA, 725 17th St. NW., Washington, DC 20503.
4. Hand Delivery: Air Docket, Room B-102, Environmental Protection Agency, 1301 Consittution Avenue, NW, Washington, DC 20460. Such deliveries are only accepted during the Docket's normal hours of operation, and special arrangements should be made for deliveries of boxed information.

Instructions. Direct your comments to Docket ID No. OAR-2003-0191. The EPA's policy is that all comments received will be included in the public docket without change and may be made available online at

http://www.epa.gov/edocket, including any personal information provided, unless the comment includes information claimed to be Confidential Business Information (CBI) or other information whose disclosure is restricted by statute. Do not submit information that you consider to be CBI or otherwise protected through EDOCKET, regulations.gov, or e-mail. The EPA EDOCKET and the Federal regulations.gov websites are “anonymous access” systems, which means EPA will not know your identity or contact information unless you provide it in the body of your comment. If you send an e-mail comment directly to EPA without going through EDOCKET or regulations.gov, your e-mail address will be automatically captured and included as part of the comment that is placed in the public docket and made available on the Internet. If you submit an electronic comment, EPA recommends that you include your name and other contact information in the body of your comment and with any disk or CD-ROM you submit. If EPA cannot read your comment due to technical difficulties and cannot contact you for clarification, EPA may not be able to consider your comment. Electronic files should avoid the use of special characters, any form of encryption, and be

free of any defects or viruses.

Docket. All documents in the docket are listed in the EDOCKET index at http://www.epa.gov/edocket. Although listed in the index, some information is not publicly available, i.e., CBI or other information whose disclosure is restricted by statute. Certain other material, such as copyrighted material, is not placed on the Internet and will be publicly available only in hard copy form. Publicly available docket materials are available either electronically in EDOCKET or in hard copy at the Air and Radiation Docket, EPA/DC, EPA West, Room B102, 1301 Constitution Ave., NW, Washington, DC. This docket facility is open from 8:30 a.m. to 4:30 p.m., Monday through Friday, excluding legal holidays. The Air and Radiation Docket telephone number is (202) 566-1742. The Public Reading Room is open from 8:30 a.m. to 4:30 p.m., Monday through Friday, excluding legal holidays. The telephone number for the Public Reading Room is (202) 566-1744.

Public Hearing. If timely requests to speak at a public hearing are received, a public hearing will be held at the EPA Office of Administration Auditorium, Research Triangle Park, North Carolina.

Persons interested in attending the public hearing must call JoLynn Collins to verify the time, date, and location of the hearing. The public hearing will provide interested parties the opportunity to present data, views, or arguments concerning these proposed amendments.

FOR FURTHER INFORMATION CONTACT: Mary Tom Kissell, Office of Air and Radiation, Emission Standards Division (C439-03), U.S. EPA, Research Triangle Park, North Carolina 27711, telephone number (919) 541-4516, fax number (919) 685-3219, e-mail: kissell.mary@epa.gov.

SUPPLEMENTARY INFORMATION:

Regulated Entities. The proposed amendments could possibly apply to a large number of industries that could be using the provisions of 40 CFR part 63, appendix C, to demonstrate compliance with an air standard. Therefore, we have not listed specific affected industries or their North American Industrial Classification System (NAICS) codes here. If you have any questions regarding the applicability of this action to a particular entity, consult the person listed in the preceding **FOR FURTHER INFORMATION CONTACT** section.

Outline. The information presented in the preamble is organized as follows:

I. Background

Appendix C to 40 CFR part 63 provides procedures for calculating F_{bio} in a biological treatment system. The appendix currently contains five procedures for determining F_{bio}: bench-top reactors, site-specific system performance data, inlet and outlet concentration data, batch tests, and multiple zone concentration measurements. Each of the procedures in appendix C are compound-specific (i.e., the individual compound fraction biodegraded (f_{bio}) is determined for each identified compound and then summed to obtain an overall F_{bio}). However, in developing the new source performance standards for wastewater sources in the synthetic organic chemical manufacturing industry, we realized that F_{bio}

determinations on an individual compound basis may be problematic for sources demonstrating compliance for large numbers of undefined VOC.

Wastewater streams from SOCMI processes can contain hundreds of organic wastewater compounds (OWWC). For these wastewater streams, identifying all (or the predominant constituents) of the OWWC would require costly analytical testing. To provide for a more cost-effective evaluation of wastewater streams with multiple OWWC, the proposed amendments to appendix C to 40 CFR part 63 add a procedure for determining an overall F_{bio} that does not require identification of specific OWWC.

II. Summary of the Proposed Amendments

The proposed amendments to appendix C to 40 CFR part 63 add a non-speciated, aerated draft tube reactor test to the existing batch test procedures described in section III.D of appendix C. The proposed non-speciated test procedure uses the same approach as the aerated reactor test, but also includes procedures that are related to evaluating individual components in a wastewater stream without having to identify these components or make separate measurements of the characteristics of the components.

The proposed test procedure relies on establishing correlations between peak areas of unidentified compounds resulting from gas chromatography (GC) analysis with the measured concentrations of the unidentified compounds in the draft tube headspace. Automated gas sampling or solid phase microextraction (SPME) fibers are used to collect samples of the gas in the headspace of the draft tube over the time period of the test. Compounds in the gas samples are measured using a gas chromatography/flame ionization detector (GC/FID).

The change in each VOC concentration in the headspace of the draft tube is related to the decrease in aqueous phase concentration of each VOC over time. This correlation is used to calculate biodegradation rates for each VOC. Also, an overall F_{bio} for the biological treatment system is calculated from the sum of the individual organic compound concentrations and individual f_{bio} values. Appendix C to 40 CFR part 63 allows the use of manual or computer-assisted methods to analyze the GC concentration data.

Today's proposed non-speciated aerated draft tube reactor test method is an appropriate addition to appendix C to 40 CFR part 63 to provide a more cost-

effective option for compliance demonstrations for activated sludge biological treatment units affected by wastewater rules regulating VOC. While we consider this to be a cost-effective option, the non-speciated method also provides an accurate procedure for demonstrating biodegradation as opposed to volatilization for an activated sludge biological unit. Although appropriate for rules such as the proposed SOCMI Wastewater NSPS that would regulate OWWC, the non-speciated aerated method may not be appropriate for other rules. In the case of the proposed SOCMI Wastewater NSPS, the regulated pollutants would be OWWC which comprise all of the organic compounds in the wastewater streams that may volatilize, i.e., compounds with a Henry's law constant greater than 0.1 atmosphere per mole fraction. For rules requiring destruction of hazardous air pollutants (HAP), other appendix C procedures are preferred because they require identification and quantification of HAP, ensuring the overall F_{bio} reflects the actual destruction of the HAP and not the average of all the organic compounds present in the wastewater. Therefore, today's proposed non-speciated aerated draft tube reactor test method may only be used to comply with rules that regulate VOC, such as

the SOCMI Wastewater NSPS.

In addition to the non-speciated aerated draft tube reactor test, the proposed amendments also make minor revisions to clarify the existing batch test procedures in section III.D of appendix C to 40 CFR part 63. We are clarifying that the batch test procedures are headspace characterization methods. Also, we are clarifying that the equilibrium verification required by the aerated reactor test must be demonstrated for one or more of the most volatile compounds to be tested for biodegradation.

III. Statutory and Executive Order Reviews

A. Executive Order 12866, Regulatory Planning and Review

Under Executive Order 12866 (58 FR 51735, October 4, 1993), EPA must determine whether the regulatory action is “significant” and, therefore, subject to review by the OMB and the requirements of the Executive Order. The Executive Order defines “significant regulatory action” as one that is likely to result in a rule that may:

(1) Have an annual effect on the economy of $100 million or more or adversely affect in a material way the economy, a sector of the economy, productivity, competition, jobs, the environment, public health or safety, or State, local, or tribal governments or

communities;

(2) create a serious inconsistency or otherwise interfere with an action taken or planned by another agency;

(3) materially alter the budgetary impact of entitlements, grants, user fees, or loan programs, or the rights and obligations of recipients thereof; or

(4) raise novel legal or policy issues arising out of legal mandates, the President's priorities, or the principles set forth in the Executive Order.

We have determined that the proposed amendments are not a "significant regulatory action" under the terms of Executive Order 12866 and do not impose any additional control requirements. The proposed amendments add an additional, potentially less-costly option for compliance demonstration for certain biological treatment units. Therefore, the proposed amendments are not subject to review by OMB.

B. Paperwork Reduction Act

The proposed amendments to appendix C to 40 CFR part 63 do not impose or change any information collection requirements. Therefore, the requirements of the Paperwork Reduction Act do not apply to the proposed

amendments.

C. Regulatory Flexibility Act

The Regulatory Flexibility Act generally requires an agency to prepare a regulatory flexibility analysis of any rule subject to notice and comment rulemaking requirements under the Administrative Procedure Act or any other statute unless the agency certifies that the rule will not have a significant impact on a substantial number of small entities. Small entities include small businesses, small government organizations, and small government jurisdictions.

For purposes of assessing the impacts of today's rule on small entities, small entity is defined as: (1) a small business with up to 1,000 employees; (2) a small governmental jurisdiction that is a government of a city, county, town, school district or special district with a population of less than 50,000; and (3) a small organization that is any not-for-profit enterprise which is independently owned and operated and is not dominant in its field.

After considering the economic impacts of today’s proposed rule on small entities, I certify that this action will not have a significant economic impact on a

substantial number of small entities. Today's proposed amendments do not increase the cost of compliance because: (1) the proposed amendments do not impose requirements independent of the proposed SOCMI Wastewater NSPS; (2) we proposed using appendix C to 40 CFR part 63 to demonstrate compliance with the proposed SOCMI Wastewater NSPS in the supplement to the proposed rule; (3) the cost of compliance demonstrations is accounted for in the proposed SOCMI Wastewater NSPS; and (4) the procedure we are proposing to add to appendix C provides another, less expensive, alternative to the procedures currently available in appendix C. We continue to be interested in the potential impacts of the proposed rule on small entities and welcome comments on issues related to such impacts.

D. Unfunded Mandates Reform Act

Title II of the Unfunded Mandates Reform Act of 1995 (URMA), Public Law 104-4, establishes requirements for Federal agencies to assess the effects of their regulatory actions on State, local, and tribal governments and the private sector. Under section 202 of the UMRA, the EPA generally must prepare a written statement, including a cost-benefit analysis, for

proposed and final rules with “Federal mandates” that may result in expenditures by State, local, and tribal governments, in the aggregate, or by the private sector, of $100 million or more in any 1 year. Before promulgating an EPA rule for which a written statement is needed, section 205 of the UMRA generally requires EPA to identify and consider a reasonable number of regulatory alternatives and adopt the least costly, most cost-effective, or least burdensome alternative that achieves the objectives of the rule. The provisions of section 205 do not apply when they are inconsistent with applicable law. Moreover, section 205 allows EPA to adopt an alternative other than the least costly, most cost-effective, or least burdensome alternative if the Administrator publishes with the final rule an explanation why that alternative was not adopted. Before EPA establishes any regulatory requirements that may significantly or uniquely affect small governments, including tribal governments, it must have developed, under section 203 of the UMRA, a small government agency plan. The plan must provide for notifying potentially affected small governments, enabling officials of affected small governments to have meaningful and timely

input in the development of EPA's regulatory proposals with significant Federal intergovernmental mandates, and informing, educating, and advising small governments on compliance with the regulatory requirements.

The EPA has determined that the proposed amendments do not contain a Federal mandate that may result in expenditures of $100 million or more for State, local, and tribal governments, in the aggregate, or the private sector in any 1 year. Thus, the proposed amendments are not subject to the requirements of section 202 and 205 of the UMRA. In addition, EPA has determined that the proposed amendments do not contain regulatory requirements that might significantly or uniquely affect small governments because the proposed amendments do not impose any additional regulatory requirements. Therefore, the proposed amendments are not subject to the requirements of section 203 of the UMRA.

E. Executive Order 13132, Federalism

Executive Order 13132 (64 FR 43255, August 10, 1999) requires EPA to develop an accountable process to ensure "meaningful and timely input by State and local officials in the development of regulatory policies that have federalism implications." "Policies that have federalism

implications" is defined in the Executive Order to include regulations that have "substantial direct effects on the States, on the relationship between the national government and the States, or on the distribution of power and responsibilities among the various levels of government."

The proposed amendments do not have federalism implications. The proposed amendments will not have substantial direct effects on the States, on the relationship between the national government and the States, or on the distribution of power and responsibilities among the various levels of government, as specified in Executive Order 13132. The proposed amendments will not impose substantial direct compliance costs on State or local governments, and they will not preempt State law. Thus, Executive Order 13132 does not apply to the proposed amendments.

F. Executive Order 13175, Consultation and Coordination with Indian Tribal Governments

Executive Order 13175 (65 FR 67249, November 9, 2000) requires EPA to develop an accountable process to ensure "meaningful and timely input by tribal officials in the development of regulatory policies that have

tribal implications."

The proposed amendments do not have tribal implications and will not have substantial direct effects on tribal governments, on the relationship between the Federal government and Indian tribes, or on the distribution of power and responsibilities between the Federal government and Indian tribes. Thus, Executive Order 13175 does not apply to the proposed amendments.

G. Executive Order 13045, Protection of Children from Environmental Health & Safety Risks

Executive Order 13045 (62 FR 19885, April 23, 1997) applies to any rule that (1) is determined to be "economically significant" as defined under Executive Order 12866, and (2) concerns an environmental health or safety risk that EPA has reason to believe may have a disproportionate effect on children. If the regulatory action meets both criteria, the EPA must evaluate the environmental health or safety effects of the planned rule on children, and explain why the planned regulation is preferable to other potentially effective and reasonably feasible alternatives considered by EPA.

The EPA interprets Executive Order 13045 as applying only to those regulatory actions that are based on health

or safety risks, such that the analysis required under section 5-501 of the Executive Order has the potential to influence the rule. The proposed amendments are not subject to Executive Order 13045 because they are based on technology performance and not on health and safety risks. Also, the proposed amendments are not "economically significant."

H. Executive Order 13211, Actions Concerning Regulations that Significantly Affect Energy Supply, Distribution, or Use

The proposed amendments are not subject to Executive Order 13211 (66 FR 28355, May 22, 2001) because they are not a significant regulatory action under Executive Order 12866 and because they will not have an adverse effect on the supply, distribution, or use of energy.

I. National Technology Transfer Advancement Act

Section 12(d) of the National Technology Transfer and Advancement Act (NTTAA) of 1995, (Public Law 104-113; 15 U.S.C. 272 note) directs EPA to use voluntary consensus standards in their regulatory and procurement activities unless to do so would be inconsistent with applicable law or otherwise impractical. Voluntary consensus standards are technical standards (e.g.,

material specifications, test methods, sampling procedures, business practices) developed or adopted by one or more voluntary consensus bodies. The NTTAA directs EPA to provide Congress, through annual reports to OMB, with explanations when an agency does not use available and applicable voluntary consensus standards.

The proposed amendments include technical standards and requirements for taking measurements. Consistent with the NTTAA, we conducted searches for applicable voluntary consensus standards that could be used in addition to the method proposed in this action by searching the National Standards System Institute (NSSN) database. We searched for methods and tests required by the proposed amendments, all of which are methods or tests previously promulgated. No potentially equivalent methods for the methods and tests in the proposal were found in the NSSN database search. Therefore, we do not propose to use any voluntary consensus standards. The search and review results are documented in Dockets No. OAR-2003-0191 and A-94-32.

List of Subjects in 40 CFR Part 63

Environmental protection, Administrative practice

and procedure, Air pollution control, Hazardous substances, Intergovernmental relations, Reporting and recordkeeping requirements.

_____
Dated:

_____
Michael O. Leavitt,
Administrator

For reasons cited in the preamble, title 40, chapter I, part 63 of the Code of Federal Regulations is amended as follows:

PART 63--[AMENDED]

1. The authority citation for part 63 continues to read as follows:

Authority: 42 U.S.C. 7401 et seq.

Appendix C to Part 63–-Determination of the Fraction Biodegraded (F_{bio}) in a Biological Treatment Unit

2. Appendix C is amended by revising Section III Procedures for Determination of F_{bio} introductory text to read as follows:

III. Procedures for Determination of F_{bio}

* * *

Procedure 4 explains three types of batch tests which may be used to estimate the first order biodegradation rate constant. * * *

* * * * *

3. Appendix C is amended by revising section III.D to read as follows:

D. Batch Tests (Procedure 4)

Three types of batch tests which may be used to determine kinetic parameters are: (1) the aerated

reactor test, (2) the sealed reactor test, and (3) the non-speciated aerated draft tube reactor test. The non-speciated aerated draft reactor test is appropriate for compliance demonstrations with rules that regulate volatile organic compounds (VOC). Where there is a limited specific list of HAP compounds of concern one of the other batch tests or procedures is preferable. The aerated reactor test is also known as the BOX test (batch test with oxygen addition). The sealed reactor test is also known as the serum bottle test. These batch tests should be conducted only by persons familiar with procedures for determining biodegradation kinetics. Detailed discussions of batch procedures for determining biodegradation kinetic parameters can be found in references 1 - 4. A detailed discussion of the non-speciated aerated draft tube reactor test can be found in reference 9.

For the batch test approaches, a biomass sample from the activated sludge unit of interest is collected, aerated, and stored for no more than 4 hours prior to testing. To collect sufficient data when biodegradation is rapid, it may be necessary to dilute the biomass sample. If the sample is to be diluted, the biomass

sample shall be diluted using treated effluent from the activated sludge unit of interest to a concentration such that the biodegradation test will last long enough to make at least six concentration measurements. It is recommended that the tests not be terminated until the compound concentration falls below the limit of quantitation (LOQ). Measurements that are below the LOQ should not be used in the data analysis. Biomass concentrations shall be determined using standard methods for measurement of mixed liquor volatile suspended solids (MLVSS) (reference 5).

The change in concentration of a test compound may be monitored by either measuring the concentration in the liquid or in the reactor headspace. The analytical technique chosen for the test should be as sensitive as possible. For the batch test procedures using headspace characterization described in this section, equilibrium conditions must exist between the liquid and gas phases of the experiments because the data analysis procedures are based on this premise. To use the headspace sampling approach, the reactor headspace must be in equilibrium with the liquid so that the headspace concentrations can be correlated with the liquid concentrations. Before the

biodegradation testing is conducted using headspace analysis, the equilibrium assumption must be verified. A discussion of the equilibrium assumption verification is given below in sections D.1 and D.2 since different approaches are required for the two types of batch tests.

To determine biodegradation kinetic parameters in a batch test, it is important to choose an appropriate initial substrate (compound(s) of interest) concentration for the test. The outcome of the batch experiment may be influenced by the initial substrate (S_o) to biomass (X_o) ratio (see references 3, 4, and 6). This ratio is typically measured in chemical oxygen demand (COD) units. When the S_o/X_o ratio is low, cell multiplication and growth in the batch test is negligible and the kinetics measured by the test are representative of the kinetics in the activated sludge unit of interest. The S_o/X_o ratio for a batch test is determined with the following equation:

$$\frac{S_o}{X_o} = \frac{S_i}{1.42\ X} \qquad \text{(Eqn. App. C-1)}$$

where:

S_o/X_o = initial substrate to biomass ratio on a COD basis

S_i = initial substrate concentration in COD units (g COD/liter)
X = biomass concentration in the batch test (g MLVSS/liter)
1.42 = Conversion factor to convert to COD units

For the batch tests described in this section, the S_o/X_o ratio (on a COD basis) must be initially less than 0.5.

1. Aerated Reactor Test. An aerated draft tube reactor may be used for the biokinetics testing (as an example see Figure 2 of appendix C). Other aerated reactor configurations may also be used. Air is bubbled through a porous frit at a rate sufficient to aerate and keep the reactor uniformly mixed. Aeration rates typically vary from 50 to 200 milliter per minute (ml/min) for a 1 liter system. A mass flow rate controller is used to carefully control the air flow rate because it is important to have an accurate measure of this rate. The dissolved oxygen (DO) concentration in the system must not fall below 2 milligram per liter (mg/liter) so that the biodegradation observed will not be DO-limited. Once the air flow rate is established, the test mixture (or compound) of interest is then injected into the reactor and the concentration of the compound(s) is monitored over time. Concentrations may

be monitored in the liquid or in the headspace. A minimum of six samples shall be taken over the period of the test. However, it is recommended to collect samples until the compound concentration falls below the LOQ. If liquid samples are collected, they must be small enough such that the liquid volume in the batch reactor does not change by more than 10 percent.

Before conducting experiments with biomass, it is necessary to verify the equilibrium assumption using one or more of the more volatile components from the list of volatile components that will be tested. A demonstration of equilibrium with the most volatile components that will be tested is expected to assure that equilibrium is also achieved with the less volatile components. The number of volatile components needed to demonstrate equilibrium depends on experimental uncertainty, literature measurement uncertainty, and the availability of previous demonstrations of equilibrium using similar equipment. If the most volatile component(s) that will be tested have a Henry’s constant of less than 0.1 (y/x), then a demonstration of equilibrium with those components is not required if a previous demonstration of equilibrium is available using similar equipment. The

equilibrium assumption can be verified by conducting a stripping experiment using the effluent (no biomass) from the activated sludge unit of interest. Effluent is filtered with a 0.45 micrometer (um) or smaller filter and placed in the draft tube reactor. Air is sparged into the system and the compound concentration in the liquid or headspace is monitored over time. This test with no biomass will provide an estimate of the Henry's law constant. If the system is at equilibrium, the Henry's law constant may be estimated with the following equation:

$$- \ln(C/C_o) = (GK_{eq}/V)t \qquad \text{(Eqn. App. C-2)}$$

where:

C	=	concentration at time, t (min)
C_o	=	concentration at t = 0
G	=	volumetric gas flow rate (ml/min)
V	=	liquid volume in the batch reactor (ml)
K_{eq}	=	Henry's law constant (mg/L-gas)/(mg/L-liquid)
t	=	time (min)

A plot of $-\ln(C/C_o)$ as a function of t will have a slope equal to GK_{eq}/V. The equilibrium assumption can be verified by comparing the experimentally determined K_{eq} for the system to literature values of the Henry's Law

constant (including those listed in this appendix). If K_{eq} does not match the Henry's law constant, K_{eq} shall be determined from analysis of the headspace and liquid concentration in a batch system.

The concentration of a compound decreases in the bioreactor due to both biodegradation and stripping. Biodegradation processes are typically described with a Monod model. This model and a stripping expression are combined to give a mass balance for the aerated draft tube reactor:

$$-\frac{ds}{dt} = \left(\frac{GK_{eq}}{V}\right) s + \left(\frac{Q_m X}{K_S + S}\right) s \quad \text{(Eqn. App. C-3)}$$

where:

s	=	test compound concentration, mg/liter
G	=	volumetric gas flow rate, liters/hr
K_{eq}	=	Henry's Law constant measured in the system, (mg/liter gas)/(mg/liter liquid)
V	=	volume of liquid in the reactor, liters
X	=	biomass concentration (g MLVSS/liter)
Q_m	=	maximum rate of substrate removal, mg/g MLVSS/hr
K_s	=	Monod biorate constant at half the maximum rate, mg/liter

Equation App. C-3 can be integrated to obtain the following equation:

$$-t = \frac{VK_s}{A} \ln\left(\frac{S}{S_o}\right) + \frac{Q_m X V^2}{AB} \ln\left(\frac{A + BS}{A + BS_o}\right) \quad \text{(Eqn. App. C-4)}$$

where:

$A = GK_{eq}K_s + Q_mVX$
$B = GK_{eq}$
s_o = test compound concentration at t=0

This equation is used along with the substrate concentration versus time data to determine the best fit parameters (Q_m and K_s) to describe the biodegradation process in the aerated reactor. If the Aerated Reactor test is used, the following procedure is used to analyze the data. Evaluate K_{eq} for the compound of interest with Form XI. The concentration in the vented headspace or liquid is measured as a function of time and the data is entered on Form XI. A plot is made from the data and attached to the Form XI. K_{eq} is calculated on Form XI and the results are contrasted with the expected value of Henry's law obtained from Form IX. If the comparison is satisfactory, the stripping constant is calculated from K_{eq}, completing Form XI. The values of K_{eq} may differ because the theoretical value of K_{eq} may not be applicable to the system of interest. If the comparison of the calculated K_{eq} from the form and the expected value of Henry's law is unsatisfactory, Form X can alternatively be used to validate K_{eq}. If the aerated reactor is demonstrated to not be at equilibrium, either modify the

reactor design and/or operation, or use another type of batch test. This equilibrium testing must only be demonstrated for one or more of the most volatile compounds to be tested for biodegradation. Once it is demonstrated that the aerated reactor achieves equilibrium, then Form IX is used to adjust published or measured Henry's law constants for the other volatile compounds to be tested.

The compound-specific biorate constants are then measured using Form XII. The stripping constant that was determined from Form XI and a headspace correction factor of 1 are entered on Form XII. The aerated reactor biotest may then be run, measuring concentrations of each compound of interest as a function of time. If headspace concentrations are measured instead of liquid concentrations, then the corresponding liquid concentrations are calculated from the headspace measurements using the K_{eq} determined on Form XI and entered on Form XII.

The concentration data on Form XII may contain scatter that can adversely influence the data interpretation. It is acceptable to curve fit the concentration data and enter the concentrations on the fitted curve instead of

the actual data. If curve fitting is used, the curve-fitting procedure must be based upon the Equation App. C-4. When curve fitting is used, it is necessary to attach a plot of the actual data and the fitted curve to Form XII.

If the stripping rate constant is relatively large when compared to the biorate at low concentrations, it may be difficult to obtain accurate evaluations of the first-order biorate constant. In these cases, either reducing the stripping rate constant by lowering the aeration rate, or increasing the biomass concentrations should be considered.

The final result of the batch testing is the measurement of a biorate that can be used to estimate the fraction biodegraded, f_{bio}. The number transferred to Form III is obtained from Form XII, line 9.

2. Sealed Reactor Test. This test uses a closed system to prevent losses of the test compound by volatilization. This test may be conducted using a serum bottle or a sealed draft tube reactor (for an example see Figure 3 of appendix C). Since no air is supplied, it is necessary to ensure that sufficient oxygen is present in the system. The DO concentration in the system must not

fall below 2 mg/liter so that the biodegradation observed will not be DO-limited. As an alternative, oxygen may be supplied by electrolysis as needed to maintain the DO concentration above 2 mg/liter. The reactor contents must be uniformly mixed, by stirring or agitation using a shaker or similar apparatus. The test mixture (or compound) of interest is injected into the reactor and the concentration is monitored over time. A minimum of six samples shall be taken over the period of the test. However, it is necessary to monitor the concentration until it falls below the LOQ.

The equilibrium assumption must be verified for the batch reactor system that depends on headspace characterization. In this case, K_{eq} may be determined by simultaneously measuring gas and liquid phase concentrations at different times within a given experiment. The equilibrium testing must only be demonstrated for one or more of the most volatile component(s) that will be tested. A constant ratio of gas/liquid concentrations indicates that equilibrium conditions are present and K_{eq} is not a function of concentration. This ratio is then taken as the K_{eq} for the specific component(s) in the test. It is not necessary to

measure K_{eq} for each experiment. If the ratio is not constant, the equilibrium assumption is not valid and it is necessary to (1) increase mixing energy for the system and retest for the equilibrium assumption, or (2) use a different type of test that does not depend on headspace characterization (for example, a collapsible volume reactor).

The concentration of a compound decreases in the bioreactor due to biodegradation according to Equation App. C-5:

$$\frac{ds}{dt} = \left[\frac{-V_1}{V_g K_{eq} + V_1}\right]\left[\left(\frac{Q_m X}{K_s + s}\right) s\right] \qquad \text{(Eqn. App. C-5)}$$

where:

s	=	test compound concentration (mg/liters)
V_l	=	the average liquid volume in the reactor (liters)
V_g	=	the average gas volume in the reactor (liters)
Q_m	=	maximum rate of substrate removal (mg/g MLVSS/hr)
K_{eq}	=	Henry's Law constant determined for the test, (mg/liter gas)/(mg/liter liquid)
K_s	=	Monod biorate constant at one-half the maximum rate (mg/liter)
t	=	time (hours)
X	=	biomass concentration (g MLVSS/liter)
s_o	=	test compound concentration at time t=0

Equation App. C-5 can be solved analytically to give:

$$t = -\frac{\left(V_g K_{eq} + V_1\right)}{V_1 Q_m X}\left[\left(s - s_o\right) + K_s \ln\left(\frac{s}{s_o}\right)\right] \quad \text{(Eqn. App. C-6)}$$

This equation is used along with the substrate concentration versus time data to determine the best fit parameters (Q_m and K_s) to describe the biodegradation process in the sealed reactor.

If the sealed reactor test is used, Form X is used to determine the headspace correction factor. The disappearance of a compound in the sealed reactor test is slowed because a fraction of the compound is not available for biodegradation because it is present in the headspace. If the compound is almost entirely in the liquid phase, the headspace correction factor is approximately one. If the headspace correction factor is substantially less than one, improved mass transfer or reduced headspace may improve the accuracy of the sealed reactor test. A preliminary sealed reactor test must be conducted to test the equilibrium assumption. As the compound of interest is degraded, simultaneous headspace and liquid samples should be collected and Form X should be used to evaluate K_{eq}. The ratio of headspace to liquid concentrations must

be constant in order to confirm that equilibrium conditions exist. If equilibrium conditions are not present, additional mixing or an alternate reactor configuration may be required.

The compound-specific biorate constants are then calculated using Form XII. For the sealed reactor test, a stripping rate constant of zero and the headspace correction factor that was determined from Form X are entered on Form XII. The sealed reactor test may then be run, measuring the concentrations of each compound of interest as a function of time. If headspace concentrations are measured instead of liquid concentrations, then the corresponding liquid concentrations are calculated from the headspace measurements using K_{eq} from Form X and entered on Form XII.

The concentration data on Form XII may contain scatter that can adversely influence the data interpretation. It is acceptable to curve fit the concentration data and enter the concentrations on the fitted curve instead of the actual data. If curve fitting is used, the curve-fitting procedure must be based upon Equation App. C-6. When curve fitting is used, it is necessary to attach a plot of the actual data and the fitted curve to Form XII.

If a sealed collapsible reactor is used that has no headspace, the headspace correction factor will equal 1, but the stripping rate constant may not equal 0 due to diffusion losses through the reactor wall. The ratio of the rate of loss of compound to the concentration of the compound in the reactor (units of per hour) must be evaluated. This loss ratio has the same units as the stripping rate constant and may be entered as the stripping rate constant on line 1 of Form XII.

If the loss due to diffusion through the walls of the collapsible reactor is relatively large when compared to the biorate at low concentrations, it may be difficult to obtain accurate evaluations of the first-order biorate constant. In these cases, either replacing the materials used to construct the reactor with materials of low permeability or increasing the biomass concentration should be considered.

The final result of the batch testing is the measurement of a biorate that can be used to estimate the fraction biodegraded, f_{bio}. The number transferred to Form III is obtained from Form XII, line 9.

The number on Form XII line 9 will equal the Monod first-order biorate constant if the full-scale system is

operated in the first-order range. If the full-scale system is operated at concentrations above that of the Monod first-order range, the value of the number on line 9 will be somewhat lower than the Monod first-order biorate constant. With supporting biorate data, the Monod model used in Form XII may be used to estimate the effective biorate constant K1 for use in Form III.

If a reactor with headspace is used, analysis of the data using Equation App. C-6 is valid only if V_l and V_g do not change more than 10 percent (i.e., they can be approximated as constant for the duration of the test). Since biodegradation is occurring only in the liquid, as the liquid concentration decreases it is necessary for mass to transfer from the gas to the liquid phase. This may require vigorous mixing and/or reducing the volume in the headspace of the reactor.

If there is no headspace (e.g., a collapsible reactor), Equation App. C-6 is independent of V_l and there are no restrictions on the liquid volume. If a membrane or bag is used as the collapsible-volume reactor, it may be important to monitor for diffusion losses in the system. To determine if there are losses, the bag should be used without biomass and spiked with the compound(s) of

interest. The concentration of the compound(s) in the reactor should be monitored over time. The data are analyzed as described above for the sealed reactor test.

3. Non-speciated aerated draft tube reactor test. This method is appropriate for compliance demonstrations with rules that regulate VOC. The aerated draft tube reactor test is used for assessing the F_{bio} for non-speciated VOC. The methods and procedures that are used with the Aerated reactor test (described in section 1 above) are also used with the non-speciated draft tube test, with the exception of special procedures that are related to the limited information available for identifying the waste components, the volatility of the components, and the amount of the components that are present in the waste. The non-speciated test method described here is based upon evaluating individual components in a waste without the need to identify the name of the component or make separate measurements of the characteristics of the components.

3.1 Purpose of the method. The following sections identify specific purposes for which the non-speciated method is used. For each purpose identified in sections 3.1.1 through 3.1.6, a correlation between the peak area

of the compound in the GC analysis and the concentration in the draft tube headspace must be available as discussed in section 3.10.

3.1.1 Henry’s law constant for each non-speciated organic compound. One run of the non-speciated method without biomass is used to obtain estimates of the Henry’s law value for each individual organic compound identified in the waste. For each volatile organic component, correlations of the vapor phase concentration and the stripping times are developed. A Henry's law value is determined for each component. See section 3.6.

3.1.2 Non-speciated organic compound concentration. One run of the non-speciated method without biomass is used to evaluate the individual organic compound concentrations in the waste. The amount of each component initially present in the waste is determined from the Henry's law value and the correlation between the peak area and the gas correlation. See section 3.9.

3.1.3 Total concentration of non-speciated organic compounds. One run of the non-speciated method without biomass is used to obtain estimates of the individual organic compound concentrations in the waste. These individual concentrations are summed to obtain the total

concentration of organic compounds. See section 3.11.

3.1.4 Biodegradation rate for each non-speciated organic compound. Two runs of the non-speciated method, one with biomass and one without biomass are used to obtain estimates of the biodegradation rate for each individual organic compound identified in the waste. The stripping rates from the run without biodegradation is compared to the air stripping run with biodegradation. The difference in the rates of removal in the two runs is used to calculate the biodegradation rate. See section 3.7.

3.1.5 Individual values of f_e and f_{bio} for each non-speciated organic compound. The use of Form III or an equivalent method is used to evaluate the fraction biodegraded (individual F_{bio}) using the Henry's law value for each component (3.6), the amount of each component (3.9), and the biodegradation rate for each component (3.7), together with the characteristics of the biotreatment unit. See section 3.12.

3.1.6 Overall F_e and F_{bio} for the total concentration of non-speciated organic compounds. The use of Form III or an equivalent method is used to evaluate the fraction biodegraded (individual f_{bio}) using the Henry's law value

for each component (3.6), the amount of each component (3.9), and the biodegradation rate for each component (3.7), together with the characteristics of the biotreatment unit.

These individual F_{bio} numbers for each of the components are used to obtain an overall F_{bio} value for the overall non-speciated waste. Non-speciated compounds with low Henry's law constants of less than 0.1 mol fraction gas per mol fraction in liquid at one atmosphere can be excluded from this summation.

A weighted summation of these individual estimates of biological and air emission removal is used to obtain an overall F_{bio} and an overall Fe. See section 3.13.

3.2 Reactor configuration. An aerated draft tube reactor is used for the biokinetics testing for the non-speciated reactor test (as an example see Figure 2 of appendix C). Other aerated reactor configurations may also be used if equivalent to the aerated draft tube reactor. Air is bubbled through a porous frit at a rate sufficient to aerate and keep the reactor uniformly mixed. A discussion of the setup and the operation of the aerated draft tube reactor is presented in Section D.1.

3.3 Reactor sampling. Concentrations of volatile

compounds are only monitored in the headspace in the non-speciated aerated draft tube reactor test. The headspace may be monitored with solid phase microextraction (SPME) fibers or with automated gas sampling. A minimum of six headspace samples shall be taken over the period of the test for each individual run and analyzed by gas chromatography. Sufficient gas samples will be taken to provide at least 3 data samples for each relevant component for each air stripping run. It is necessary to collect enough samples to quantify the characteristics of the individual volatile compound peaks in the system; therefore, in some cases it is possible to reduce the total number of headspace samples by sampling more frequently at the beginning of the run.

3.4 Reactor equilibrium verification. It is necessary to verify the equilibrium assumption for the non-speciated aerated draft tube reactor test as discussed in section D.1, using Equation C-2.

A plot of $-\ln(C/C_o)$ as a function of t will have a slope equal to GK_{eq}/V. Verification of equilibrium can be performed initially and periodically with a set of known volatile compounds with known Henry's law constants. The selection of compounds should represent the most volatile

compounds in the waste stream (at least as great as the experimentally measured Henry’s law constants for the top 5 percent of the non-speciated components, or alternatively with Henry’s law constants of 300 y/x). Experimentally measured Henry’s law values are available from the WATER7 (or any subsequent update to the model) data base for a number of compounds. In addition, the compounds that are selected for the verification of equilibrium should be included in the determination of the SPME fiber partition factor. Verification of equilibrium in the non-speciated aerated draft tube reactor test under each set of operating conditions is important because accurate measurement of the Henry's law constant is necessary to permit accurate characterization of non-speciated peaks. Non-speciated compound peaks that demonstrate Henry's law constants less than 0.1 (y/x) in the test are excluded from the analysis. If the aerated draft tube reactor cannot be demonstrated to be at equilibrium, modify the reactor design and/or operation.

3.5 Two reactor runs. The concentration of a compound in the bioreactor is measured in the headspace in two different runs, first with air stripping only and then second with both biodegradation and air stripping. A

first order biodegradation rate model is used to model the biodegradation in the aerated draft tube reactor. Since the measurement of the first order biodegradation rate constant is a function of concentration, it is important to have concentrations of non-speciated compounds in this test that closely represent the conditions in the full-scale biodegradation unit that you are evaluating. Since the components and concentrations are generally unknown for this non-speciated method, samples of actual wastewater should be obtained from the applicable location in the full-scale facility, or as close to these conditions as practicable, such as a sample of wastewater from a pilot plant, a full-scale process from another site, etc. This model and a stripping expression are combined to give a mass balance for the aerated draft tube reactor:

$$-\frac{ds}{dt} = \left(\frac{GK_{eq}}{V}\right)s + K_1 X_s \qquad \text{(Eqn. App. C-7)}$$

where:

s	=	test compound concentration, mg/liter
G	=	volumetric gas flow rate, liters/hr
K_{eq}	=	Henry's Law constant measured in the system, (mg/liter gas)/(mg/liter liquid)
V	=	volume of liquid in the reactor, liters

X = biomass concentration (g MLVSS/liter)
K_1 = first order biodegradation rate constant, liter/g MLVSS/hr

Equation App. C-7 can be integrated to obtain the following equation:

$$In\left(\frac{Peakarea_t}{Peakarea_o}\right) = -\left(\frac{GK_{eq}}{V} + K_1X\right)t \qquad \text{(Eqn. App. C-8)}$$

where:

$Peakarea_t$ = the area of the non-speciated compound peak at time t,
$Peakarea_o$ = the area of the non-speciated compound peak at the beginning of the run,
GK_{eq}/V = contribution to the slope from stripping only, and
K_1X = contribution to the slope from biodegradation.

If ln(Peakarea) is plotted on the y axis and t is plotted on the x axis, the data should form a straight line with a slope that equals the negative of the terms in parenthesis on the right of Equation App. C-8 and the intercept of this line on the y axis equals ln ($Peakarea_o$).

A discussion of Equation App. C-8 is provided in reference 9. This equation is used to analyze the two stripping runs, with and without biodegradation. Evaluate the slope for each non-speciated peak for both the run

without biodegradation and the run with biodegradation.

3.6 Henry's law constants. To evaluate the Henry's law constant for each unspeciated VOC, you obtain the slope for the run without biodegradation and then equate this slope (with a negative value) to $-GK_{eq}/V$. The value of K_{eq} is then equal to the product of the negative of the slope and V, divided by G.

3.7 Biodegradation rate constant. To evaluate the first order biorate constant, use the slope for each non-speciated peak for the run without biodegradation and subtract the corresponding slope of the non-speciated peak with biodegradation. This difference equals K_1X. The value of K_1 that is determined in this manner is used to characterize the biodegradation rate under the conditions in the full-scale biodegradation unit that you are evaluating.

3.8 Accuracy concerns. The non-speciated compound peak data may contain scatter that can adversely influence the data interpretation. In the case of significant data scatter for a specific compound that will limit the ability to determine the difference in slopes from the two runs, it is possible to use conventional statistics to estimate the accuracy of the difference in slopes. When

it is not possible to demonstrate a significant difference in the slopes of the two runs for a non-speciated compound, the value of K_1 is set to zero. A negative value of K_1 is never used. If the specific compound of concern has a statistically significant negative value of K_1, this can be an indication of the formation of the compound as a byproduct and is reported as an anomalous result. It is necessary to provide documentation of data and calculations.

If the stripping rate constant is relatively large when compared to the biorate, it may be difficult to obtain an accurate evaluation of the first-order biorate constant. In these cases, either reducing the stripping rate constant by lowering the aeration rate, or increasing the biomass concentrations should be considered. If the aeration rate is changed, the equilibrium assumption will have to be verified again. Equilibrium conditions are typically more difficult to obtain at greater aeration rates, but lower aeration rates could result in difficulty in achieving equilibrium conditions due to poorer mixing.

3.9 <u>The concentration of each compound</u>. The amount of each individual non-speciated organic compound is calculated by measuring the initial area of the

chromatographic peak of the individual compound, $Peakarea_{o,}$ the ratio of the peak area to the gas phase concentration, F, the SPME fiber partition factor, $K_{fiber,}$ and the partition coefficient, $K_{eq.}$ The $Peakarea_o$ is the intercept of the line with the y axis (plot of ln Peakarea vs. time). If automatic gas sampling is used for the analysis, a representative calibration of the gas chromatographic peak area and the gas phase concentration is required, and a correlation for the fiber partition factor is not used because the SPME method is not used. For complex chemicals with relatively poor biodegradation rates, it may be necessary to modify the procedure using multiple columns or detectors.

The equation used for the SPME method is as follows:

$$C_L = \frac{P_A}{FK_{eq}K_{fiber}} \qquad \text{(Eqn. App. C-9)}$$

where:

C_L = the concentration of the component in the water, (mg/L),

P_A = the integrated peak area of the component in the gas chromatograph, (area counts),

K_{eq} = the ratio of the concentration of the component in the headspace to the concentration of the component in the water, (mg/L per mg/L),

K_{fiber} = the ratio of the mass on the extraction fiber to the concentration of the component in the

headspace, (mg per mg/L), and
F = the ratio of the peak area to the mass on the extraction fiber, (area counts/mg).

The equation used for the automatic headspace sampling alternative is as follows:

$$C_L = \frac{P_A}{FcK_{eq}} \qquad \text{(Eqn. App. C-10)}$$

where the symbols are defined above, and Fc is the ratio of the peak area count to the concentration in the gas phase, (mg/L). This number depends on the sampling and analysis setup.

3.10 SPME fiber partition correlation. If automatic gas sampling is used, it is not necessary to account for SPME fiber partition effects, but it is necessary to use gas chromatographic calibration factors for the compounds of interest. Reference 9 presents additional details on the use of gas chromatographic calibration factors and SPME fiber partition factors.

The SPME fiber partition factor is obtained by preparing an aqueous solution or solutions with known compounds of varying volatility and chemical characteristics that are representative of the waste stream of concern. The detector peak areas and retention

times are then obtained with the SPME method for these known compounds. The mass of compound is calculated from the area counts of the GC compound peak, and the concentration in the headspace is calculated from the Henry's law factor and the known liquid concentration. The fiber partition factor K_{fiber} is the ratio of the mass of compound to the concentration in the headspace at equilibrium with the aqueous solution. A correlation is then obtained between the value of K_{fiber} and the retention time of the detector response.

The SPME fiber partition factor correlation for a series of petrochemical compounds that is provided in Figure 4 of reference 9 can be used with verification of the correlation with a few compounds if the chemicals in that correlation are representative of the waste stream of concern. The fiber recovery of the compound is correlated with the volatility (aqueous Henry's law constant) as a result of the experimental measurements of the headspace concentrations by the fiber extraction method.

If some characterization is available for the waste stream of concern, such as a compound identification of more than 25 percent of the major compounds present in the waste, it is recommended that selected members of these

identified compounds are included in the measurements for the determination of the site-specific SPME fiber partition factor correlation.

In some cases, after concluding the non-speciated method runs for the waste with and without biomass, the SPME partition factor correlation may appear to be inappropriate for the waste stream. Some of the reasons for this could include incorrect compound concentration for a known compound, incorrect concentration ratios of known compounds, or test data outside the applicable range of the correlation. When there are problems with the SPME partition factor correlation, the correlation may be improved without the need to rerun the non-speciated method runs for the waste with and without biomass.

If, unlike the petroleum compound set evaluated in reference 9, you are unable to obtain a single correlation for use in interpreting the data that you obtain from this method, you should consider the use of two or more correlations with multiple correlations and multiple detectors/fiber types. A discussion of the methods used in this multiple correlation technique alternative is outside the scope of this discussion. This alternative of more than one correlation should not be used without

supporting experimental investigations to verify the technical approach that you are using. The EPA Method 25D describes the use of two different types of gas chromatograph detectors to more completely characterize the compounds in the waste. You may wish to consider the use of automatic direct headspace sampling in the case of difficulty with identifying adequate SPME correlations.

3.11 Calculation of the total non-speciated compound concentration. The measured individual organic compound concentrations are summed to obtain the total non-speciated compound concentration. Certain compounds may be excluded from this total. Examples of components that may be excluded from the total summation procedures are the following:

- Components that are present in the vapor phase in concentrations too low to measure.
- Components that are identified and have specific regulatory exclusion.
- Components that have gas chromatographic retention times that are substantially greater than can be considered characteristic of volatile components.

3.12 Calculation of f_e and f_{bio} for each compound. The site specific biodegradation unit characteristics are

used with the measured values of the compound Henry's law value and the biodegradation first order rate constant to estimate f_e and f_{bio} for each compound.

3.13 Calculation of the overall f_e and F_{bio} for the total volatile waste components. The individual organic compound concentrations are used with individual values of f_e and f_{bio} to obtain the total biological removal and the total air emission removal from the treatment unit. In the case of an ideal stirred tank reactor, the amount of each component entering the reactor is calculated by multiplying the flow rate of the waste (m^3/s) by the concentration (g/m^3) to obtain the individual loading rate (g/s). For each compound that is not excluded, the individual loading is summed to obtain the total loading. The overall biological removal is the sum of the products of the individual loading rate (g/s) and the individual value of f_{bio}. The overall air removal is the sum of the products of the individual loading rates (g/s) and the individual values of fe. The overall f_{bio} value is the ratio of the overall biological removal to the total loading. The overall f_e value is the ratio of the overall air emissions loss to the total loading.

Reference 9 presents examples of the use of the above

procedures to evaluate the fraction biodegraded for two types of biotreatment units.

3.14 Computer assisted calculations. It is possible to use computer assisted data acquisition and data analysis in order to reduce the extensive labor requirements to perform the above procedures manually. You may use either manual methods, electronic spreadsheets, or compiled programs that can directly import the gas chromatographic computer files. Present the results for each non-speciated component, the summary of the weighted average F_{bio} using each relevant component, and supporting quality assurance information. The slope and intercept of the correlation curve, the correlation coefficient, and the number of data points used for the correlation are examples of supporting quality assurance information.

4. Quality Control/Quality Assurance (QA/QC). A QA/QC plan outlining the procedures used to determine the biodegradation rate constants shall be prepared and a copy maintained at the source. The plan should include, but may

not be limited to:

1. A description of the apparatus used (e.g., size,

volume, method of supplying air or oxygen, mixing, and sampling procedures) including a simplified schematic drawing.

2. A description of how biomass was sampled from the activated sludge unit.

3. A description of how biomass was held prior to testing (age, etc.).

4. A description of what conditions (DO, gas-liquid equilibrium, temperature, etc.) are important, what the target values are, how the factors were controlled, and how well they were controlled.

5. A description of how the experiment was conducted, including preparation of solutions, dilution procedures, sampling procedures, monitoring of conditions, etc.

6. A description of the analytical instrumentation used, how the instruments were calibrated, and a summary of the precision for that equipment.

7. A description of the analytical procedures used. If appropriate, reference to an ASTM, EPA or other procedure may be used. Otherwise, describe how the procedure is done, what is done to measure precision, accuracy, recovery, etc., as appropriate.

8. A description of how data are captured, recorded,

and stored.

9. A description of the equations used and their solutions, including a reference to any software used for calculations and/or curve-fitting.

3. Appendix C is amended by revising section III.E to read as follows:

E. Multiple Zone Concentration Measurements (Procedure 5)

Procedure 5 is the concentration measurement method that can be used to determine the f_{bio} for units that are not thoroughly mixed and thus have multiple zones of mixing. As with the other procedures, proper determination of f_{bio} must be made on a system as it would exist under the rule. For purposes of this calculation, the biological unit must be divided[1] into zones with uniform characteristics within each zone. The number of zones that is used depends on the complexity of the unit. Reference 8, "A Technical Support Document for the Evaluation of Aerobic Biological Treatment Units with Multiple Mixing Zones," is a source for further information concerning how to determine the number of zones that should be used for evaluating your unit. The

[1] This is a mathematical division of the actual unit; not addition of physical barriers.

following information on the biological unit must be available to use this procedure: (1) basic unit variables such as inlet and recycle wastewater flow rates, type of agitation, and operating conditions; (2) measured representative organic compound concentrations in each zone and the inlet and outlet; and (3) estimated mass transfer coefficients for each zone.

The estimated mass transfer coefficient for each compound in each zone is obtained from Form II using the characteristics of each zone. A computer model may be used. If the Water7 model or the most recent update to this model is used, then use Form II-A to calculate KL. The TOXCHEM or BASTE model may also be used to calculate KL for the biological treatment unit, with the stipulations listed in procedure 304B. Compound concentration measurements for each zone are used in Form XIII to calculate the f_{bio}. A copy of Form XIII is completed for each of the compounds of concern treated in the biological unit.

4. Appendix C is amended by revising equation C-7 in section IV to read as follows:

IV. Calculation of F_{bio}

* * * * *

$$F_{bio} = \frac{\sum_{i=1}^{n} (f_{bio_i} \times M_i)}{\sum_{i=1}^{n} M_i} \qquad \text{(Eqn. App. C-11)}$$

where:

M = compound specific average mass flow rate of the organic compounds in the wastewater (Mg/Yr)

n = number of organic compounds in the wastewater

* * * * *

5. Appendix C is amended by revising the references to read as follows:

1. Rajagopalan, S., R. van Compernolle, C.L. Meyer, M.L. Cano, and P.T. Sun. "Comparison of methods for determining biodegradation kinetics of volatile organic compounds." Wat. Env. Res. 70: 291-298.

2. Ellis, T.G., D.S. Barbeau, B.F. Smets, C.P.L. Grady, Jr. 1996. Respirometric technique for determination of extant kinetic parameters describing biodegradation. Wat. Env. Res. 68: 917-926.

3. Pitter, P. and J. Chudoba. Biodegradability of

Organic Substances in the Aquatic Environment. CRC Press, Boca Raton, FL. 1990.

4. Grady, C.P.L., B. Smets, and D. Barbeau. Variability in kinetic parameter estimates: A review of possible causes and a proposed terminology. Wat. Res. 30 (3), 742-748, 1996.

5. Eaton, A.D., et al. eds., Standard Methods for the Examination of Water and Wastewater, 19th Edition, American Public Health Association, Washington, DC, 1995.

6. Chudoba P., B. Capdeville, and J. Chudoba. Explanation of biological meaning of the So/Xo ratio in batch cultivation. Wat. Sci. Tech. 26 (3/4), 743-751, 1992.

7. Technical Support Document for Evaluation of Thoroughly Mixed Biological Treatment Units. November 1998.

8. Technical Support Document for the Evaluation of Aerobic Biological Treatment Units with Multiple Mixing Zones. July 1999.

9. Saterbak, A., M.L. Cano, M.P. Williams, M.E. Huot, I.A. Rhodes, R. van Compernolle, and C.C. Allen, 1999. Aerated draft tube reactor test for assessing non-speciated volatile organic compound (VOC) biodegradation

in activated sludge. Proceedings of the Water Environment Federation 72nd Annual Conference and Exposition, New Orleans, LA, October 9-13.