PEER REVIEW OF EPA'S HAZARDOUS WASTE IDENTIFICATION RULE RISK ASSESSMENT MODEL

ANAEROBIC BIODEGRADATION RATES OF ORGANIC CHEMICALS IN GROUNDWATER: A SUMMARY OF FIELD AND LABORATORY STUDIES

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NOTE

This report was prepared by Eastern Research Group, Inc. (ERG), an EPA contractor, under Contract Number 68-W-99-001. The report presents comments provided by peer reviewers on the *Anaerobic Biodegradation Rates Of Organic Chemicals In Groundwater: A Summary Of Field And Laboratory Studies* document that is part of EPA's Hazardous Waste Identification Rule risk assessments.

The comments presented in this report have been compiled by topic and by individual peer reviewer. As EPA requested, this report provides the peer review comments exactly as they were submitted to ERG. Also attached are the original comments submitted by each individual reviewer.

PEER REVIEW - ANAEROBIC BIODEGRADATION RATES
OF ORGANIC CHEMICALS IN SATURATED ZONE

A.   INTRODUCTION AND BACKGROUND

The U.S. Environmental Protection Agency (EPA) identifies under Subtitle C of the Resource Conservation and Recovery Act (RCRA) hazardous wastes that pose threat to human health and the environment. Wastes applicable under the Hazardous Waste Identification Rule (HWIR) were those designated as hazardous because they were listed, or had been mixed with, derived from, or contained the listed wastes. Under the HWIR proposal, waste generators of listed wastes that could meet the new exemption-level criteria defined by the HWIR methodology, would no longer be subject to the hazardous waste management system requirements specified under Subtitle C of RCRA for those wastes. Basically, this would establish a risk-based "floor" for low risk hazardous wastes that would encourage pollution prevention, waste minimization, and the development of innovative waste treatment technologies. The purpose of the rulemaking is to reduce possible over-regulation arising from the older "mixture" and "derived-from" rules promulgated earlier.

The "mixture" rule and the "derived-from" rule were promulgated as part of the first comprehensive regulatory program for the management of hazardous wastes under RCRA in May of 1980. The mixture rule defined as a hazardous waste any solid waste that is mixed with one or more listed hazardous wastes, and the derived-from rule labeled as hazardous waste any solid waste generated from the treatment, storage, or disposal of a listed hazardous waste. Both rules were are considered important definitions in regulating the disposal of hazardous wastes consistent with reducing risk to human health and the environment; however, since they apply regardless of the concentration or mobility of hazardous constituents associated with the solid wastes, the potential for over-regulation is a possibility. One of the primary purposes of HWIR is to provide a risk-based methodology for identifying possible instances of over-regulation, and to provide an avenue for safe relief from the Subtitle C disposal regulations as appropriate.

EPA uses environmental fate and transport models in the risk assessment approach used to support the development and implementation of regulations for solid and hazardous waste management, under the Resource Conservation and Recovery Act (RCRA) so as to protect, the human health and the environment. These models are implemented on a nationwide basis for one chemical constituent at a time utilizing the Monte Carlo procedure. The output from models forms the basis for the risk assessment of waste management practices. EPA's Composite Model for Leachate Migration with Transformation Products (**EPACMTP**) is the subsurface fate and transport model which EPA's Office of Solid Waste implements on a nationwide basis using the Monte Carlo analysis techniques. The Agency also is developing a multimedia, mutipathway, and multireceptor risk assessment (3MRA) model for use for identifying wastes based on constituent-specific exit levels for low risk hazardous wastes. The 3MRA model is based on the regional site-based approach used in EPACMTP and the subsurface fate and transport modules in 3MRA model were extracted from EPACMTP. The procedure for the implementation of these models requires nationally representative distributions of first order biodegradation rates.

EPA uses anaerobic biodegradation rates in the subsurface fate and transport model. The Agency considers that although anaerobic biodegradation is not the slowest activity, it is less

likely that data collected under anaerobic conditions would lead to an overestimation of the degradation rate. In general, the concentrations of oxygen and nitrate are insignificant in ground waters that have been impacted with leachate from landfills. This condition results from prior microbial consumption of oxygen or nitrate that was supported by the electron acceptor demand of materials in the landfill leachate. Consequently, the rate of supply of oxygen and nitrate into impacted ground waters is slow. The rate of supply is limited, by mass transfer processes from ground water that has not been impacted (and as a consequence has oxygen and nitrate available), into the plume impacted with leachate from a landfill. As a result, the only microbial processes that are generally available for biodegradation of hazardous organic compounds in ground water impacted with leachate from landfills are the processes of iron reduction, sulfate reduction, and methanogenesis (Krumholz et. al., 1996). Therefore, EPA considers selected rate constants provided by laboratory and field studies that were conducted under iron reducing, sulfate reducing, or methanogenic conditions to be rate constants that are appropriate for use in EPACMTP. EPA does not consider rate constants provided by laboratory and field studies that were conducted under aerobic or nitrate reducing conditions to be appropriate for use in EPACMTP.

EPA developed a protocol to generate national distributions of anaerobic biodegradation rates for organic chemicals for use in the model (53 FR 22300, June 15, 1988). The protocol requires collecting samples from six sites: three sites in the northern half of the United States; and three sites located in the southern half of the country. Ideally, these six sites will represent the various pH and redox environments prevalent in the country. However, the protocol has not been implemented widely by the industry so far. Meanwhile, many laboratory and field studies on the anaerobic biodegradation of chemicals have become available since the protocol was developed more than ten years ago. Suggestions were made to critically evaluate these studies and incorporate the results in modeling. Therefore, EPA convened a workshop in Atlanta, Georgia, on anaerobic biodegradation of organic chemicals in 1997. Representatives from academia, industry and the EPA participated in discussions. Written comments from an environmental group were also considered at the workshop. Based on these discussions and other inputs from EPA scientists, the Agency developed criteria for the evaluation of the field as well as laboratory studies. The criteria are listed in Appendices A and B (laboratory and field studies, respectively) of the EPA report.

At the workshop, industry representatives provided a report summarizing field and laboratory studies on anaerobic biodegradation of organic compounds. The report entitled "Anaerobic Biodegradation of Organic Chemicals in Groundwater: A Summary of Field and Laboratory Studies" was prepared for the American Petroleum Institute (API), and other industrial organizations, by the Syracuse Research Center, 1997. The criteria used by Syracuse Research Corporation is presented in Appendix C of the EPA report. Since the criteria used by Syracuse Research Center to review research papers was less stringent than the criteria decided upon at the workshop, EPA conducted a second review of the Syracuse Research Center Report. In addition, EPA conducted a literature review to collect additional studies on biodegradation of various organic chemicals (both laboratory as well as field). For purposes of this report, biodegradation is defined as "removal of a compound from ground water through biological activity". Only studies which were conducted with aquifer materials under anaerobic conditions were selected for review. In addition studies carried out on mixtures of compounds, and studies where the aquifer material was seeded with microorganisms from other sources were not

included. The studies were then evaluated to see if they satisfied the proposed EPA criteria. Biodegradation rates from studies which met the proposed criteria were used to develop a distribution of first order rates for potential use as input to the EPA's subsurface fate and transport model.

Information from the tables in Appendix F of the EPA report for each compound is used in the subsurface Monte-Carlo fate and transport modeling. In a Monte-Carlo realization, a site is selected along with the subsurface temperature and the pH. Then an anaerobic biodegradation rate is picked from the appropriate cell of the table, randomly corresponding to either a methanogenic or sulfate reducing environment. The rate is then used for that site in the analysis. For the next Monte Carlo site realization, the model then selects a rate from the table based on the temperature, pH, and either methanogenic or sulfate reducing environment at random with replacement. The process is repeated for the total number of Monte Carlo realizations.

B.   MATERIALS OFFERED FOR REVIEW

Materials to be Reviewed According to the Charge:

US EPA, 1999. Anaerobic Biodegradation Rates of Organic Chemicals in Groundwater: A summary of Field and Laboratory Studies for HWIR99.

Supporting Documents for information Purposes:

1.   Syracuse Research Center. Anaerobic Biodegradation of organic Chemicals in Groundwater: A Summary of Field and Laboratory Studies, SRC TR-97-0223F, 1997.

2.   53 FR 22300, 40 CFR Section 795.54. Anaerobic microbiological transformation rate data for chemicals in the subsurface environments, June 15, 1988.

REFERENCE:

Krumholz, L.R., Caldwell, M.E., and Suflita, J.M., Biodegradation of 'BTEX' hydrocarbons under anaerobic conditions, pages 61 through 99 in: "Bioremediation: Principles and Applications", R. L. Crawford and D. L. Crawford, Cambridge University Press, 1966.

C.   CHARGE TO THE REVIEW PANEL

As stated earlier that the intended purpose of HWIR99 is to provide a generic national-level risk assessment tool to determine which wastes are most appropriately handled in Federal-regulated, hazardous waste management units (Subtitle C) and which wastes should be handled in State-regulated non-hazardous waste management units (Subtitle D).   The review panelists should focus their efforts on providing informed answers to the questions posed below, with specific recommendations for improvements identified that are practical and implementable

within about six months, if at all possible. In so doing, it is asked that each panelist address the following component aspects of the general questions:

1)   There are many ways to categorize the anaerobic biodegradation rates for use in implementing a subsurface fate and transport model on a nationwide basis . The categorization developed in our report was designed for use in the model for practical purposes using the Monte Carlo technique to substitute for the data which is to be developed using the EPA's protocol published in the Federal Register. Is this categorizing of anaerobic biodegradation rate data adequate for the intended use?

2)   The anaerobic biodegradation rates presented in EPA's report are based on the available information at the time report was prepared. Are these rates for specific chemicals appropriate or are there other verifiable data available to supplement the data? Please provide references/citations for your suggested data sources.

3)   Is the consideration of first order anaerobic biodegradation rates appropriate for our practical purpose of implementing the model on a nation-wide basis utilizing the Monte Carlo procedure?

4)   Due to lack of actual field data on anaerobic biodegradation rates, we are compelled to consider data developed in the laboratory using the criteria presented in the report. Is the laboratory data for use in the model, which is intended to simulate field conditions, an adequate substitute for practical purposes to support our nation-wide modeling efforts for risk assessments?

<div align="center">**Reviewer Comments Summary Report for the**</div>

General Comments:

Dr. Alexander: This reviewer has very, very serious and major objections to the entire approach used here for predicting rates of anaerobic biodegradation. These objections are based both on theoretical grounds and on the basis of the actual data.

To evaluate actual data, I have examined the tables and figures (i.e., the actual data) in papers cited on p. G-2 (no. 3, 13, and 14), G-3 (no. 26 and 27), G-4 (no. 3 and 5), G-5 (no.10 and 22), G-6 (no. 28, 29, and 3), G-7 (no. 9, 12, and 16), G-8 (no. 3), G-9 (no. 3, 7, and 10), G-10 (no. 19 and 20), G-11 (no. 2 and 13), G-12 (no. 3), G-13 (no. 8, 9, 3 and 6), G-14 (no. 1), G-15 (no. 17), G-16 (no. 1 on vinyl chloride and no. 3 and 7 on phenol), G-18 (no. 1 and 5 on DCP and no. 3 on PCP), G-19 (no. 4 for fluorene and no. 5 and 6 for methylnaphthalene), G-20 (no. 1 and 13), and G-22 (no. 1 and 2 for pyridine and no. 1 for styrene). Note that some of the same references are on more than one page.

Note also that the sulfite reference on p. G-13 is not in Environ. Sci. Technol. but in Environ. Toxicol. Chem.

Many papers have dealt with the theoretical basis for the kinetics of biodegradation, and one chapter of this reviewer's book (pp. 73-104 in M. Alexander, *Biodegradation and Bioremediation*, 1999, 2nd. Edition) is concerned specifically with kinetics. The chapter also has more than 100 references on theory, and it summarizes published articles.

From a theoretical viewpoint, two general patterns of kinetics exist: growth-linked and nongrowth-linked. If a compound supports growth, the kinetics of bioremediation are **not first order**. Microbial growth does not follow first-order kinetics. Benzene, toluene, xylenes, ethylbenzene, and phenol generally support growth, and when these compounds were tested (in the references I read and cited above), the kinetics were never first order.

Other compounds are cometabolized; i.e., their utilization does not support growth. Their biodegradation **may be** first order. First-order kinetics were found in one study of 1,1,1-trichloroethane and one of TCE but not in other studies. The actual data are thus in agreement with the theory.

To use some value for a first-order rate constant is thus often incorrect, misleading and will lead to erroneous conclusions on the concentrations and persistence of compounds not degraded by first-order kinetics.

I herewith summarize my examination of some of the data:

Probably growth-linked: ref. 13, 14, and 26 for benzene; ref. 16 for ethylbenzene; ref.

<div align="center">1</div>

19 for o-xylene; ref. 17 for TCE (unexpected); ref. 3 for phenol.

Not first-order: ref. 3, 5, 10, and 22 for toluene; 3 and 9 for ethylbenzene; 3 for m-xylene; 3 and 7 for o-xylene; 3 for p-xylene; 8 for tetrachloroethylene; 3 for PCP; 8 for naphthalene, and 2 for pyridine.

Zero order: ref. 1 for vinyl chloride (sometimes) and 7 for phenol.

First-order: ref. 2 for chloroethane and 1 for TCE.

Two-compartment (two first-order rates): ref. 3 for carbon tetrachloride.

Insufficient data for even a rough kinetic analysis: ref. 27 for benzene, 28 for toluene, 12 for ethylbenzene, 20 for o-xylene, 9 for tetrachloroethylene, 6 for TCE, 1 for DCP, 4 for fluorene, 5 and 6 for methylnaphthalene, 13 for naphthalene, 1 for pyridine and 1 for styrene.

If the disappearance is linked to growth and the elapsed time for half of a compound to disappear is used to obtain a value for the presumed half-life in first-order kinetics, the estimated time to reach an appreciable percentage of loss of the chemical can be very seriously in error. That error becomes increasingly great if the bacterial growth that caused the degradation is increasingly slow.

Another serious error introduced by arbitrarily and universally using first-order kinetics is evident in the published curves (based on actual data) that show a biphasic pattern, especially if there is little or no degradation in the second phase. Does one use the rate from the initial phase, which will incorrectly predict loss of the chemical when it is no longer being degraded? Does one assume the second phase to represent the overall pattern and then overestimate the concentration with time?

Introduction and Background. The text (p. 2) correctly states that oxygen and nitrate can essentially be ruled out as electron acceptors because they would be quickly reduce and mass transfer would be slow. The text states that iron and sulfate are appropriate electron acceptors to be considered. However, the supply of sulfate is limited and its regeneration requires either mass transfer from an adjacent site or a source of oxygen since its regeneration is typically aerobic (just like nitrate). So data with sulfate as an electron acceptor should be excluded if the data with nitrate are not to be considered.

With regard to iron as an electron acceptor, the text ignores the fact that oxidized iron, although often abundant, exists in many forms, including Fe_2O_3, Fe_3O_4, $FeOOH$, $Fe(OH)_3$, $Fe(OH)_2(I)$, $Fe(OH)(II)$, $Fe(III)$ as well as ferric-humic complexes. Fe_2O_3 (hematite), $FeO(OH)$ (goethite), Fe_3O_4 (magnetite), $Fe(OH)_3$, ferric-humic complexes, and other iron compounds exist at moderate pH values and, at low pH, $Fe(III)$, $Fe(OH)(II)$, and $Fe(OH)_2(I)$. Fe in the lattice of clay minerals (e.g., biotite and chlorite) may be totally unavailable. The availability of these as electron acceptors to microorganisms, their concentrations, their water solubility, and the rate of their interconversions are essentially unknown, and few of the published biodegradability studies have considered iron speciation in groundwaters and aquifer solids. The issue is particularly acute because the solubility of trivalent iron is so low (less than 0.01 mg/L above pH 4.8), and thus Fe in solids must be utilized or solubilized at a rapid rate to sustain biodegradation.

2

The text correctly points out the key role of temperature and pH in affecting biodegradation rates. It ignores, however, the toxicity of the chemical to the microorganisms carrying out the biodegradation, and toxicity also affects rate. This is determined by the concentration of the chemical, which could be an input to the assessment. It also does not consider possible toxicity resulting from the degradation; e.g., changes in pH, accumulation of sulfide as a result of sulfate reduction, possible ferrous toxicity at low pH and the appearance of organic products.

Table 2.1. One can only be dismayed when rate constants are given with 1, 2, 3, 4 and even 5 significant figures. What is meant by the "reaction product" column: unknown, not determined in these reports, or what?

Appendix B. A criterion is suggested as a decline by 1 or preferably 2 orders of magnitude. Nevertheless, few of the references cited (which I read) show a decline of even a single order of magnitude.

Given the range of rate constants in appendix D (and even no biodegradation) under conditions that are presumably identical (at least in terms that are listed and presumed to be the key controlling factors; i.e., temperature, pH, and identity of the electron acceptor), major controlling factors obviously are not being considered. Should establishing these factors not be a major priority for any future evaluations? Can one meaningfully make predictions (i.e., most likely estimates) by relying on the median value (as done on Table 2.1) when the observed rate constants range from zero to greater than 100 times the median value?

Table 2.1, p. 2. Typographical error: Acetic acid, Trichlorofl**ou**romethane.

Granting that values may be needed now for regulatory decision, two courses of action seem appropriate. First, state the uncertainties (some of which are given above) in the text of this document. Second, mount a program to find out why the shapes of the disappearance curves (i.e., first, second, or zero order or more complex kinetics) occur and why the rates are so different even when pH, temperature and electron acceptors are the same.

Dr. Farrell: In this review, I will review the report text and tables as they are presented and will discuss shortcomings and omissions. Finally, I will address the specific questions asked for in the "Charge to the Review Panel".

Review of text The following numbered items are a series of comments which follow the order of the text of the report.

Comments on the Introduction

1) The Introduction is helpful but could be improved on. I believe this would be a good place to put a more complete explanation of the EPACMTP model and how it will use the distributions of anaerobic biodegradation rates. A good knowledge of what the model is

supposed to do will help enormously in trying to evaluate whether the compilation of biodegradation rates will be useful in producing accurate predictions from the model. To say that the model uses Monte Carlo analysis is not a sufficient picture of how and where the collected data fit into the picture. The last paragraph of the report (last paragraph of Section 2.0) adds a little information but together with the material in the introduction is not sufficient to tell the reader how and to what end the reaction rates will be utilized.

2) In the fourth paragraph of the Introduction, the EPA protocol to generate national distributions of biodegradation rates is discussed, and we are referred to the Federal Register for the protocol. The protocol asks for tests at three sites at about 10 degrees C and three sites at 20 degrees C. The three sites at each temperature are to be at a pH less than 6, 6 to 8, and above 8. There is no opportunity to choose a range of redox levels (presumably all should be at a redox associated with sulfate and iron reducing conditions or methanogenic conditions of the site). At each site, degradation rates are to be determined at three concentrations of the chemical of concern. The protocol requires that the nature of the soil be determined and the heterotrophic , methanogenic and sulfate-reducing microbiological densities be determined. The point I am getting at is that three points at one temperature and three points at a temperature 10 degrees higher does not make a national distribution.   It may be possible to construct a good predictive model for expected rate constants for the nation from these data, but those attempting to apply the model would have to have a great deal of information about their site, particularly about its redox condition and the biomass types and densities. In my opinion, it is unlikely that the raw rate data collected by the protocol could possibly represent a national distribution. But then, since it has not been done, and very likely will not be done, we do not have an issue that we can address. However, the discussion is relevant when we think (see later - my Items 9 and 10) about what is the utility of the data on rates that are shown in the report.

3) The remainder of Paragraph 4 of the Introduction is reasonable and useful.

Comment on Objective

4) There is no clear objective statement in the report, and there should be. There are some important things missing from the report (they will be discussed later), and possibly the authors' statement of their objectives would explain their absence. Even if the authors were not asked to include the missing items, they should be included now to improve the utility of the report.

Comments on Review of Biodegradation Studies

5) In Review of Biodegradation Studies (Section 2), Table 2.1 (Summary of Rate Constants) is discussed only in the first paragraph. There are a couple of things that could be added to the table to improve its utility. I think it would be helpful to the reader if

half-lives, calculated from the median value of the rate constant, were given. For example, for the median rate for toluene of 0.02 day^{-1}, the half life is 35 days, whereas for ethylbenzene (median rate is 0.0031 day^{-1}), the half life is 223 days. The differences in rates becomes more palpable. It would also be helpful if the number of observations that make up the distribution be included in the table. For some of the chemicals the number is very small, so standard deviation is suspect. Also, it would make it clear whether average rates or individual measurements (from Table F) went into the median and standard deviation calculation (at least in some cases, the standard deviations in Table 2.1 were calculated from all the observations rather than from the averages). I recognize that Table 2.1 is primarily descriptive (the real meat of the report is in Tables D, E, and F), but it would not hurt to make the table clear.

It should be noted too that the standard deviation assumes a normal distribution. Examination of the rate constants (e.g., I looked at benzene) shows that it is most likely log normal. The use of the standard deviation implies a normal distribution of the rate constants. This is questionable when the variability is large and the median value is close to zero. A standard deviation without a mean is essentially worthless. It cannot be applied to a median. A look at the distribution of values obtained for benzene shows that the distribution is badly skewed. The tabulation below shows the range of rate constants versus the number in each range:

0.000 - < 0.005	17	0.025 - < 0.030	0
0.005 - < 0.010	8	0.030 - < 0.035	2
0.010 - < 0.015	5	0.035 - < 0.040	0
0.015 - < 0.020	1	0.040 - < 0.045	0
0.020 - < 0.025	1	0.045 - < 0.050	1
		0.050 - < 0.055	1
		> 0.055	1 (0.071)

If it is assumed that the 17 measurements of zero are not really zero but are distributed from zero to 0.005, the data can be plotted as a log normal cumulative distribution (see attached Figure 1 - the fit is poor but much better than a normal distribution). The mean is about 0.00145 and the log standard deviation is 0.54. The median of the arithmetic distribution (0.0, see Table 2-1) is obviously a more conservative figure than the mean of the log normal distribution, but the standard deviation of the normal distribution is very misleading. The spread (antilog of the log standard deviation) is 3.45. The range in which 95 % of the observations are expected to fall (about +/- 2 standard deviations) is 0.00021 to 0.010. This gives a more realistic picture of the scatter in the data than stating that the median is zero and the standard deviation is 0.0152. Actually, most of the data in Table F appear to be closer to a log normal than a normal distribution. Of course, when there are only a few points, one cannot tell anything about the distribution.

6) In Paragraph 1 of Section 2, the authors combine Tables D (lab studies) with Table E

(field studies) to produce Table F (the sum of the contents of Tables D and E). At some later point in the Results Section, it is said that Table F is to be used in the Monte Carlo fate and transport modeling. There is no justification given for melding the data of Table D and E into Table F, and the authors should try to justify this action. Examination of the data for those few compounds when there are more than a few points shows that there is a reasonable justification for combining the tables. In the attached drawing (my Figure 2), I have plotted the rate constants for four compounds for which there were numerous data points. Lab and field data were compared, and results at less than and greater than 15 degrees C were identified. Looking first at benzene, there seems to be no difference between lab and field data, so there would be no objection to combining the data. Actually there seems to be no difference between data for less than or greater than 15 degrees C for any of the compounds. Considering the great spread of the data, this is not surprising since the expected temperature effect is probably less than a factor of two. There are other interesting observations that could be made from this figure. The field results for ethylbenzene appear to be higher than the lab results, whereas for trichloroethylene the opposite is true. The data for toluene show close agreement between laboratory and field except for the total absence of very low rates in the field tests. For ethylbenzene and toluene, the higher rate constants for the field tests than for the lab tests could be the result of aerobic decomposition, which is very hard to avoid in field tests. On the other hand, the lower rate constants for the field tests as compared to the lab tests for trichloroethylene may be due to the fact that trichloroethylene degrades aerobically very slowly if at all (Bouwer, E.J. et al., Envir. Sci. & Tech. 15 596-599 [1981]). Exposure to air that might occur in field tests would not cause decomposition and would inhibit anaerobic processes, producing lower rate constants. The point to this extended discussion is that an in-depth examination of the assembled data could produce very helpful scientific information.

7) The screening procedure described in Section 2 greatly reduced the number of available studies from the numbers tabulated in the Syracuse report (it would be desirable to indicate the fraction of survivors that met the strict screening criteria). With all the work of screening to get this "elite" collection of data, it certainly is relevant to scrutinize the data (as noted in Item 6) and get out of it all that is possible.

8) The purpose of the screening was to get usable distribution of reaction rate constants for use in the EPACMTP model. The authors evidently are leaving it to someone else to decide whether the collection of data for each of the compounds listed provides a reasonable distribution of reaction rates. It is evident that the distribution is adequate for not more than a half-dozen of the compounds. Should not the authors make an assessment of the adequacy of the distributions (including their criteria for this assessment) ?

9) In Paragraph 2 of Section 2, the authors describe their selection procedure for screening out inappropriate results from the Syracuse report and any other new data. The

procedure followed the prescriptions given in Appendix A. There is no information on biomass. There is no indication whether the samples were taken close in to the source of the plume (where the effective biomass might be expected to be higher, or far out in the plume where the concentration of nutrients and chemical of concern would be lower). The age of the exposure would be of help. Actually, this extra information is not needed for the EPACMTP model, so the authors cannot be faulted for not going beyond what is needed.

The EPACMTP model has the potential to do a good job of predicting what occurs at individual sites if it could use other parameters to adjust the rate constants. This kind of information could come out of the results of application of the EPA protocol discussed in Item 2 above. It might be desirable to apply the protocol to one of the chemicals of concern, such as benzene, to see if such rate constant could be adjusted to take account of the effect of type and nature of biomass, OR potential, and nutrient concentration. This, of course, cannot be done in the required framework of six months, but it should be a target for the future.

10) The great spread in results for the compounds is very interesting. In my opinion, it suggests that the protocol devised by EPA and described in the Federal Register (FR 53 No. 15, 22320-22323) is not the best approach for getting a distribution of rate constants, and that this random approach - getting data from a great variety of sites - may actually be better for giving a true picture of the variation in rates to be expected in the country. The protocol describes an excellent scheme for getting information on the fundamental biodegradation in the subsurface environment, and should be done at least in part. It is doubtful that the six sites chosen will provide enough information to get a population of reaction rates suitable for use in the EPACMTP model.

11) The serious problem of substances whose breakdown products are toxic and may degrade very slowly does not receive any attention. For some compounds this is not anticipated to be a problem, but it could be a very serious problem for chlorinated organic compounds. The literature probably gives enough information so that a user of any reaction rate distributions for the mother compound is made aware that a dangerous product may be formed. I believe the report should alert the reader to those compounds where a problem of this nature is likely.

12) Several of my problems with the report would not be problems if the authors had attempted to include objectives, discussion of results, conclusions and recommendations sections to their report. Why they would not include these sections mystifies me.

Minor problems

13) In Table F, a reference is needed for 1-methylnaphthalene (p F-41)

14) In Table E, < pH 6 is missing. Temperature is missing (p E-17)

15) The relationship of the chemicals examined in the report and presented in the tables to significant lists of toxic or hazardous compounds is not mentioned.

16) It is strange to see some of the compounds in the list. For example, acetic acid is listed, and there are no data satisfying the EPA protocol. Nevertheless, it is well known that acetic acid is easily degraded by methanogenic bacteria. The conversion of acetic acid to carbon dioxide and methane by methanogens is a principal pathway in the anaerobic digestion of complex wastes.

17) I found some inconsistencies between Table F and Tables D and E. For example, I noted the reference numbers in Table D and Table E and checked to see if they appeared in Table F (I believe they should appear in Table F since it is the sum of Tables D and E). I did this for benzene and toluene. For benzene, Reference 29 (methanogenic) is in Table E but it does not appear in Table F. Reference 19 (methanogenic) is in Table D but not in Table F. Reference 28 (methanogenic) is in Table F but not in either Table D or E. I found no problems with the tables for toluene. There may be a simple explanation for these inconsistencies, but it may be worth reviewing all of the tables for such glitches.
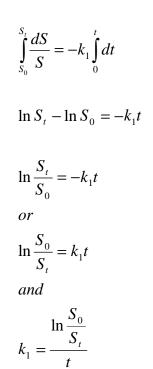
Dr. Yonge: An error was noted on page 4 and 5 of the Syracuse Research Corporation report that involves the development of equation 4 and 6. Although a minor point, equation 3 should be expressed as

$$\frac{dS}{dt} = -k_0$$ instead of

$$\frac{dS}{dt} = k_0$$ Similarly, equation 5 should be expressed as

$$\frac{dS}{dt} = -k_1 S$$

To illustrate the need for the negative sign, integration and algebraic manipulation of the first order rate equation yields the following.

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$$\int_{S_0}^{S_t} \frac{dS}{S} = -k_1 \int_0^t dt$$

$$\ln S_t - \ln S_0 = -k_1 t$$

$$\ln \frac{S_t}{S_0} = -k_1 t$$

or

$$\ln \frac{S_0}{S_t} = k_1 t$$

and

$$k_1 = \frac{\ln \dfrac{S_0}{S_t}}{t}$$

Charge 1: *There are many ways to categorize the anaerobic biodegradation rates for use in implementing a subsurface fate and transport model on a nationwide basis . The categorization developed in our report was designed for use in the model for practical purposes using the Monte Carlo technique to substitute for the data which is to be developed using the EPA's protocol published in the Federal Register. Is this categorizing of anaerobic biodegradation rate data adequate for the intended use?*

Dr. Alexander: The categorization of anaerobic biodegradation-rate data is not adequate for the intended use. My reasons are given above, but I do repeat the proviso in the paragraph immediately above.

("Granting that values may be needed now for regulatory decision, two courses of action seem appropriate. First, state the uncertainties (some of which are given above) in the text of this document. Second, mount a program to find out why the shapes of the disappearance curves (i.e., first, second, or zero order or more complex kinetics) occur and why the rates are so different even when pH, temperature and electron acceptors are the same.")

Dr. Farrell: I believe that using the EPACMTP model for its intended purpose is all right, and that first order rate constants are useful for this purpose. I am not sure about the use of the first order rate constants as calculated when there is a long latency period. The tabulated rate constants are for the rate after the latency period is over. It is likely that if the plume has reached some underground position and has been present for at least as long as the latency period, it should be all right to use the rate constants. That could be a substantial time after the site was

producing leachate, because, as we know, the plume front advances slowly.

Dr. Yonge: This approach to defining rate data for use in EPACMTP is appropriate for the intended purpose. The criteria for evaluating laboratory and field studies should yield rate data that is applicable for use in the predictive model. Furthermore, the selection of conservative (low) rate data affords a factor of safety and the Monte Carlo technique results in a statistically valid method of selection.

Charge 2:   *The anaerobic biodegradation rates presented in EPA's report are based on the available information at the time report was prepared. Are these rates for specific chemicals appropriate or are there other verifiable data available to supplement the data? Please provide references/citations for your suggested data sources.*

Dr. Alexander: The rates for specific chemicals are not appropriate when the information comes from a test in which the kinetics are clearly shown to deviate appreciably from first order. I do not know of additional data.

Dr. Farrell: I do not have any new references/citations to suggest to add to the ones in the report.

Dr. Yonge: For the chemicals I am familiar with, the rates are appropriate. Since the literature review responsible for the compilation of the rate data appears to have been concluded in 1997, I performed a "Current Contents" literature review to evaluate and update the rate data in the EPAABR report. This review covered the latter half of 1997 through 1999. Over 90 articles were recovered from the search query (search terms: "anaerobic biodegradation" and "leachate AND biodegradation".

After reviewing abstracts and reading selected articles, two articles were found to conform to the majority of the criteria for evaluating rate data (Appendix A and B of EPAABR) (Bradley and Chapelle, 1999; Bjerg, P.L., et al., 1999). The article authored by Bjerg et al., was particularly interesting since concentration-time data was collected in both laboratory batch and *in situ* microcosm experiments for five chemicals referenced in EPAABR. The *in situ* experiments were performed at different positions within a landfill leachate plume and the laboratory experiments were performed using soil and groundwater collected from within the plume. Temperature and redox potential was controlled to represent groundwater conditions in the laboratory experiments, abiotic controls were used in both experimental protocol, and the degradation experiments were carried out for up to 550 days (79 weeks).

Although first order rate constants were not presented in the article, the concentration - time data in the figures were adequate to estimate the first order rate constant, *k*, through application of Equation 1. Rate constants calculated in this manner are presented in Table 1 for toluene, m/p xylene, trichloroethene (TCE), perchloroethene (PCE), and ethylbenzene. These

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data indicate that, with the exception of TCE, data collected in a leachate plume environment, are within the range of those reported in the EPAABR report. The TCE rate data are greater than the range of values reported in EPAABR, however, this would yield a conservative modeling result with regard to risk. Thus, the results of Bjerg, et al., validate the first order rate constants reported in the EPAABR report for the five chemicals evaluated.

$$k = \frac{\ln\left(\dfrac{S_0}{S_t}\right)}{\Delta t}$$ (1)

where,

k = first order rate constant
S_0 = initial concentration
S_t = concentration at time t
Δt = time interval from S_0 to S_t

Table 1. First order kinetic rate constants from Bradley and Chapelle, 1999 and Bjerg, P.L., et al., 1999. Italicized values are from the EPAABR report.

Compound	Min (day^{-1})	Max (day^{-1})	Median (day^{-1})
Toluene	**0.018**	**0.041**	**0.039**
	0	0.186	0.02
m/p xylene			0.013
	0	0.17	0.0052
TCE[1]	**0.05**	**0.07**	**0.060**
	0.0082	0.04	0.0016
PCE[2]			0.071
	0	0.071	0.00186
Ethylbenzene	**0.00067**	**0.0035**	**0.0021**
	0	0.46	0.0031

[1] tricholoroethene
[2] perchloroethene

It is interesting to note that although toluene and PCE yielded relatively high first order rate constants following the initiation of degradation, they exhibited long lag periods (50 to 300 days for toluene and 100 days for PCE). This indicates the importance of carrying out degradation experiments for extended periods.

Charge 3:   *Is the consideration of first order anaerobic biodegradation rates appropriate for our practical purpose of implementing the model on a nation-wide basis utilizing the Monte Carlo procedure?*

Dr. Alexander: The consideration of first-order anaerobic-biodegradation rates is often not appropriate for implementing the model.

Dr. Farrell: I believe that the use of the first order biodegradation rates in the EPACMTP model is satisfactory for establishing the distribution of performances that is to be expected at the leaching sites in the country. This of course presumes that the model gets a correct distribution of reaction rates. In my opinion, of the 44 compounds listed in Table 2, there is enough information on perhaps a half-dozen of them for barely adequate distributions. There is a long way to go before there is any comprehensive answer for the numbers of toxic or hazardous compounds of concern.

Dr. Yonge: Based on the intended use, the application of a standard first order rate term is completely appropriate. No less error would be incurred by attempting to use a Monod-based expression, as the simplifying assumptions made to describe the subsurface environment are likely to be the controlling factor in deviations of predicted from actual values (chemical concentrations).

Charge 4:   *Due to lack of actual field data on anaerobic biodegradation rates, we are compelled to consider data developed in the laboratory using the criteria presented in the report. Is the laboratory data for use in the model, which is intended to simulate field conditions, an adequate substitute for practical purposes to support our nation-wide modeling efforts for risk assessments?*

Dr. Alexander: In the absence of actual field date, the use of relevant laboratory data is an adequate substitute for practical purposes.

Dr. Farrell: I have addressed this issue in my Item 6 above. It appears that for some compounds the field data and the laboratory data can be merged without introducing substantial error, thus expanding the number of elements in the distribution. This may not be true in all cases. When the laboratory results are distributed in a higher range than the field test results (e.g., consider the case of trichloroethylene discussed above), I would give greater weight to the field results. It is reasonable to expect that field results will be less accurate than higher average rates than the laboratory results, but when results spread out over a 10 or 50-fold range, the differences in accuracy are dwarfed by other factors. Consequently, there is no strong reason to prefer lab results over field results.

       If judgements are made as to whether field data, lab data or the combination of the two are closer to the truth, the distributions will be reasonable and can be used in the model. As noted earlier, the distributions will be very wide. The range of the predicted concentrations at some

point in the plume will consequently also be very wide. They may be so wide that they are not of much value for the regulators or the regulated community. The distributions can be made more accurate and their range narrowed if other factors (probably the most significant are biomass type and density) could be included to adjust the rate constants. Possibly, nutrient concentration in the leaching liquid would be a correlating factor that would reduce the spread of the distributions. Of course, this would mean that an assessment of a site could not be made without this kind of information for the site.

I do not believe that at this state of knowledge the EPACMTP model can be used to predict a specific outcome at a site unless an experimentally determined rate constant is available for that site.

Dr. Yonge: The use of carefully controlled laboratory experimental data is an appropriate substitute for field data. We have collected batch reactor (serum bottles) kinetic data in our laboratory to define anaerobic biological reduction rate constants for CrVI. The rate constants have then been applied in a modeling effort to design continuous flow column experiments. The model predictions were excellent. These and other results lead me to believe that the kinetic data are "transferable" to the field. The more significant challenge (and limiting factor) is in adequately defining the physical and chemical characteristics of the subsurface.

Recommended Improvements:

Dr. Farrell: I believe that most of the suggestions I have made can be implemented within 6 months. Obviously collection of new data cannot be completed in this time frame. In the long term, work should be supported directed towards including parameters in the model that will adjust the rate constants for the particular situations at the various sites.

Items that can and should be implemented within 6 months are:

* Item 1 - explain EPACMTP better.

* Items 2, 9, and 10 - These items support the conclusion that the approach suggested of developing distributions from existing and future data from field and lab studies, and not exclusively from data developed using the EPA protocol, is good. Continue on this path.

* Items 4 and 12 - The authors should expand the report and include objective, discussion of results, conclusions and recommendations. Many of the points I have raised would have been addressed if the authors took this standard approach to reporting results of an investigation.

* Items 6 and 11 - Critically analyze the data in the tables, draw conclusions and make recommendations on how to meld the lab and field data, and how to address toxic breakdown products. If the authors explain carefully how they came to their conclusions,

others who use the report will be able to assess what they say and make their own judgements. Discussion by the authors of fine points and points the reader might overlook will improve the utility of the report.

* Item 5 - The authors should make Table 2.1 clearer. Standard deviation based on a normal distribution seems faulty. Even median and range (along with the number of observations - range requires that) would be better than standard deviation. The data should be looked at, such as in Figure 2. Looking at data is very useful.

* Items 7 and 8 - These items are related to Items 4 and 12. They must examine their data to properly complete Items 4 and 12.

* Items 13-17 - These minor items should be corrected.

* Item 18 - Experts familiar with application of the EPACMTP model should look into the implications of the latency period as it affects model results.

* Item 21 - The authors carefully assess the issue and should make recommendations on the best way to merge field and lab data.

Literature Cited:

Dr. Yonge:
Bjerg, P.L., Rugge, K., Cortsen, J., Nielsen, P.H., Christensen, T.H., 1999. Degradation of aromatic and chlorinated aliphatic hydrocarbons in the anaerobic part of the Grinsted Landfill leachate plume: In situ microcosm and laboratory batch experiments, Ground Water, 37: (1) 113-121.

Bradley, P.M. and Chapelle, F.H., 1999. Methane as a product of chloroethene biodegradation under

ATTACHMENT A

Peer Review of "Anaerobic Biodegradation Rates Of Organic Chemicals In Saturated Zone" by:

Martin Alexander
Cornell University

REVIEW

ANAEROBIC BIODEGRADATION RATES

Martin Alexander

November 1999

This reviewer has very, very serious and major objections to the entire approach used here for predicting rates of anaerobic biodegradation. These objections are based both on theoretical grounds and on the basis of the actual data.

To evaluate actual data, I have examined the tables and figures (i.e., the actual data) in papers cited on p. G-2 (no. 3, 13, and 14), G-3 (no. 26 and 27), G-4 (no. 3 and 5), G-5 (no.10 and 22), G-6 (no. 28, 29, and 3), G-7 (no. 9, 12, and 16), G-8 (no. 3), G-9 (no. 3, 7, and 10), G-10 (no. 19 and 20), G-11 (no. 2 and 13), G-12 (no. 3), G-13 (no. 8, 9, 3 and 6), G-14 (no. 1), G-15 (no. 17), G-16 (no. 1 on vinyl chloride and no. 3 and 7 on phenol), G-18 (no. 1 and 5 on DCP and no. 3 on PCP), G-19 (no. 4 for fluorene and no. 5 and 6 for methylnaphthalene), G-20 (no. 1 and 13), and G-22 (no. 1 and 2 for pyridine and no. 1 for styrene). Note that some of the same references are on more than one page.

Note also that the sulfite reference on p. G-13 is not in Environ. Sci. Technol. but in Environ. Toxicol. Chem.

Many papers have dealt with the theoretical basis for the kinetics of biodegradation, and one chapter of this reviewer's book (pp. 73-104 in M. Alexander, *Biodegradation and Bioremediation*, 1999, 2nd. Edition) is concerned specifically with kinetics. The chapter also has more than 100 references on theory, and it summarizes published articles.

From a theoretical viewpoint, two general patterns of kinetics exist: growth-linked and nongrowth-linked. If a compound supports growth, the kinetics of bioremediation

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are **not first order**. Microbial growth does not follow first-order kinetics. Benzene, toluene, xylenes, ethylbenzene, and phenol generally support growth, and when these compounds were tested (in the references I read and cited above), the kinetics were never first order.

Other compounds are cometabolized; i.e., their utilization does not support growth. Their biodegradation **may be** first order. First-order kinetics were found in one study of 1,1,1-trichloroethane and one of TCE but not in other studies. The actual data are thus in agreement with the theory.

To use some value for a first-order rate constant is thus often incorrect, misleading and will lead to erroneous conclusions on the concentrations and persistence of compounds not degraded by first-order kinetics.

I herewith summarize my examination of some of the data:

Probably growth-linked: ref. 13, 14, and 26 for benzene; ref. 16 for ethylbenzene; ref. 19 for o-xylene; ref. 17 for TCE (unexpected); ref. 3 for phenol.

Not first-order: ref. 3, 5, 10, and 22 for toluene; 3 and 9 for ethylbenzene; 3 for m-xylene; 3 and 7 for o-xylene; 3 for p-xylene; 8 for tetrachloroethylene; 3 for PCP; 8 for naphthalene, and 2 for pyridine.

Zero order: ref. 1 for vinyl chloride (sometimes) and 7 for phenol.

First-order: ref. 2 for chloroethane and 1 for TCE.

Two-compartment (two first-order rates): ref. 3 for carbon tetrachloride.

Insufficient data for even a rough kinetic analysis: ref. 27 for benzene, 28 for toluene, 12 for ethylbenzene, 20 for o-xylene, 9 for tetrachloroethylene, 6 for TCE, 1 for DCP, 4 for fluorene, 5 and 6 for methylnaphthalene, 13 for naphthalene, 1 for pyridine and 1 for styrene.

If the disappearance is linked to growth and the elapsed time for half of a

compound to disappear is used to obtain a value for the presumed half-life in first-order kinetics, the estimated time to reach an appreciable percentage of loss of the chemical can be very seriously in error. That error becomes increasingly great if the bacterial growth that caused the degradation is increasingly slow.

Another serious error introduced by arbitrarily and universally using first-order kinetics is evident in the published curves (based on actual data) that show a biphasic pattern, especially if there is little or no degradation in the second phase. Does one use the rate from the initial phase, which will incorrectly predict loss of the chemical when it is no longer being degraded? Does one assume the second phase to represent the overall pattern and then overestimate the concentration with time?

Introduction and Background. The text (p. 2) correctly states that oxygen and nitrate can essentially be ruled out as electron acceptors because they would be quickly reduce and mass transfer would be slow. The text states that iron and sulfate are appropriate electron acceptors to be considered. However, the supply of sulfate is limited and its regeneration requires either mass transfer from an adjacent site or a source of oxygen since its regeneration is typically aerobic (just like nitrate). So data with sulfate as an electron acceptor should be excluded if the data with nitrate are not to be considered.

With regard to iron as an electron acceptor, the text ignores the fact that oxidized iron, although often abundant, exists in many forms, including Fe_2O_3, Fe_3O_4, $FeOOH$, $Fe(OH)_3$, $Fe(OH)_2(I)$, $Fe(OH)(II)$, $Fe(III)$ as well as ferric-humic complexes. Fe_2O_3 (hematite), $FeO(OH)$ (goethite), Fe_3O_4 (magnetite), $Fe(OH)_3$, ferric-humic complexes, and other iron compounds exist at moderate pH values and, at low pH, $Fe(III)$, $Fe(OH)(II)$, and $Fe(OH)_2(I)$. Fe in the lattice of clay minerals (e.g., biotite and chlorite) may be totally unavailable. The availability of these as electron acceptors to microorganisms, their concentrations, their water solubility, and the rate of their interconversions are essentially unknown, and few of the published biodegradability

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studies have considered iron speciation in groundwaters and aquifer solids. The issue is particularly acute because the solubility of trivalent iron is so low (less than 0.01 mg/L above pH 4.8), and thus Fe in solids must be utilized or solubilized at a rapid rate to sustain biodegradation.

The text correctly points out the key role of temperature and pH in affecting biodegradation rates. It ignores, however, the toxicity of the chemical to the microorganisms carrying out the biodegradation, and toxicity also affects rate. This is determined by the concentration of the chemical, which could be an input to the assessment. It also does not consider possible toxicity resulting from the degradation; e.g., changes in pH, accumulation of sulfide as a result of sulfate reduction, possible ferrous toxicity at low pH and the appearance of organic products.

Table 2.1. One can only be dismayed when rate constants are given with 1, 2, 3, 4 and even 5 significant figures. What is meant by the "reaction product" column: unknown, not determined in these reports, or what?

Appendix B. A criterion is suggested as a decline by 1 or preferably 2 orders of magnitude. Nevertheless, few of the references cited (which I read) show a decline of even a single order of magnitude.

Given the range of rate constants in appendix D (and even no biodegradation) under conditions that are presumably identical (at least in terms that are listed and presumed to be the key controlling factors; i.e., temperature, pH, and identity of the electron acceptor), major controlling factors obviously are not being considered. Should establishing these factors not be a major priority for any future evaluations? Can one meaningfully make predictions (i.e., most likely estimates) by relying on the median value (as done on Table 2.1) when the observed rate constants range from zero to greater than 100 times the median value?

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Table 2.1, p. 2. Typographical error: Acetic acid, Trichlorofl**ou**romethane.

Granting that values may be needed now for regulatory decision, two courses of action seem appropriate. First, state the uncertainties (some of which are given above) in the text of this document. Second, mount a program to find out why the shapes of the disappearance curves (i.e., first, second, or zero order or more complex kinetics) occur and why the rates are so different even when pH, temperature and electron acceptors are the same.

Charge to the Review Panel

The charge listed four questions. The answers are below.

1.   The categorization of anaerobic biodegradation-rate data is not adequate for the intended use. My reasons are given above, but I do repeat the proviso in the paragraph immediately above.

2.   The rates for specific chemicals are not appropriate when the information comes from a test in which the kinetics are clearly shown to deviate appreciably from first order. I do not know of additional data.

3.   The consideration of first-order anaerobic-biodegradation rates is often not appropriate for implementing the model.

4.   In the absence of actual field date, the use of relevant laboratory data is an adequate substitute for practical purposes.

ATTACHMENT B

Peer Review of "Anaerobic Biodegradation Rates Of Organic Chemicals In Saturated Zone" by:

Joseph Farrell
Environmental Consultant

Review of the report "Anaerobic Biodegradation Rates of Organic chemicals in Groundwater: A Summary of Field and Laboratory Studies"

In this review, I will review the report text and tables as they are presented and will discuss shortcomings and omissions. Finally, I will address the specific questions asked for in the "Charge to the Review Panel".

Review of text The following numbered items are a series of comments which follow the order of the text of the report.

Comments on the Introduction

1) The Introduction is helpful but could be improved on. I believe this would be a good place to put a more complete explanation of the EPACMTP model and how it will use the distributions of anaerobic biodegradation rates. A good knowledge of what the model is supposed to do will help enormously in trying to evaluate whether the compilation of biodegradation rates will be useful in producing accurate predictions from the model. To say that the model uses Monte Carlo analysis is not a sufficient picture of how and where the collected data fit into the picture. The last paragraph of the report (last paragraph of Section 2.0) adds a little information but together with the material in the introduction is not sufficient to tell the reader how and to what end the reaction rates will be utilized.

2) In the fourth paragraph of the Introduction, the EPA protocol to generate national distributions of biodegradation rates is discussed, and we are referred to the Federal Register for the protocol. The protocol asks for tests at three sites at about 10 degrees C and three sites at 20 degrees C. The three sites at each temperature are to be at a pH less than 6, 6 to 8, and above 8. There is no opportunity to choose a range of redox levels (presumably all should be at a redox associated with sulfate and iron reducing conditions or methanogenic conditions of the site). At each site, degradation rates are to be determined at three concentrations of the chemical of concern. The protocol requires that the nature of the soil be determined and the heterotrophic , methanogenic and sulfate-reducing microbiological densities be determined. The point I am getting at is that three points at one temperature and three points at a temperature 10 degrees higher does not make a national distribution.   It may be possible to construct a good predictive model for expected rate constants for the nation from these data, but those attempting to apply the model would have to have a great deal of information about their site, particularly about its redox condition and the biomass types and densities. In my opinion, it is unlikely that the raw rate data collected by the protocol could possibly represent a national distribution. But then, since it has not been done, and very likely will not be done, we do not have an issue that we can address. However, the discussion is relevant when we think (see later - my Items 9 and 10) about what is the utility of the data on rates that are shown in the report.

3) The remainder of Paragraph 4 of the Introduction is reasonable and useful.

<u>Comment on Objective</u>

4) There is no clear objective statement in the report, and there should be. There are some important things missing from the report (they will be discussed later), and possibly the authors' statement of their objectives would explain their absence. Even if the authors were not asked to include the missing items, they should be included now to improve the utility of the report.

<u>Comments on Review of Biodegradation Studies</u>

5) In Review of Biodegradation Studies (Section 2), Table 2.1 (Summary of Rate Constants) is discussed only in the first paragraph. There are a couple of things that could be added to the table to improve its utility. I think it would be helpful to the reader if half-lives, calculated from the median value of the rate constant, were given. For example, for the median rate for toluene of 0.02 day^{-1}, the half life is 35 days, whereas for ethylbenzene (median rate is 0.0031 day^{-1}), the half life is 223 days. The differences in rates becomes more palpable. It would also be helpful if the number of observations that make up the distribution be included in the table. For some of the chemicals the number is very small, so standard deviation is suspect. Also, it would make it clear whether average rates or individual measurements (from Table F) went into the median and standard deviation calculation (at least in some cases, the standard deviations in Table 2.1 were calculated from all the observations rather than from the averages). I recognize that Table 2.1 is primarily descriptive (the real meat of the report is in Tables D, E, and F), but it would not hurt to make the table clear.

It should be noted too that the standard deviation assumes a normal distribution. Examination of the rate constants (e.g., I looked at benzene) shows that it is most likely log normal. The use of the standard deviation implies a normal distribution of the rate constants. This is questionable when the variability is large and the median value is close to zero. A standard deviation without a mean is essentially worthless. It cannot be applied to a median. A look at the distribution of values obtained for benzene shows that the distribution is badly skewed. The tabulation below shows the range of rate constants versus the number in each range:

0.000 - < 0.005	17	0.025 - < 0.030	0
0.005 - < 0.010	8	0.030 - < 0.035	2
0.010 - < 0.015	5	0.035 - < 0.040	0
0.015 - < 0.020	1	0.040 - < 0.045	0
0.020 - < 0.025	1	0.045 - < 0.050	1
		0.050 - < 0.055	1

| | > 0.055 | 1 (0.071) |

If it is assumed that the 17 measurements of zero are not really zero but are distributed from zero to 0.005, the data can be plotted as a log normal cumulative distribution (see attached Figure 1 - the fit is poor but much better than a normal distribution). The mean is about 0.00145 and the log standard deviation is 0.54. The median of the arithmetic distribution (0.0, see Table 2-1) is obviously a more conservative figure than the mean of the log normal distribution, but the standard deviation of the normal distribution is very misleading. The spread (antilog of the log standard deviation) is 3.45. The range in which 95 % of the observations are expected to fall (about +/- 2 standard deviations) is 0.00021 to 0.010. This gives a more realistic picture of the scatter in the data than stating that the median is zero and the standard deviation is 0.0152. Actually, most of the data in Table F appear to be closer to a log normal than a normal distribution. Of course, when there are only a few points, one cannot tell anything about the distribution.

6) In Paragraph 1 of Section 2, the authors combine Tables D (lab studies) with Table E (field studies) to produce Table F (the sum of the contents of Tables D and E). At some later point in the Results Section, it is said that Table F is to be used in the Monte Carlo fate and transport modeling. There is no justification given for melding the data of Table D and E into Table F, and the authors should try to justify this action. Examination of the data for those few compounds when there are more than a few points shows that there is a reasonable justification for combining the tables. In the attached drawing (my Figure 2), I have plotted the rate constants for four compounds for which there were numerous data points. Lab and field data were compared, and results at less than and greater than 15 degrees C were identified. Looking first at benzene, there seems to be no difference between lab and field data, so there would be no objection to combining the data. Actually there seems to be no difference between data for less than or greater than 15 degrees C for any of the compounds. Considering the great spread of the data, this is not surprising since the expected temperature effect is probably less than a factor of two. There are other interesting observations that could be made from this figure. The field results for ethylbenzene appear to be higher than the lab results, whereas for trichloroethylene the opposite is true. The data for toluene show close agreement between laboratory and field except for the total absence of very low rates in the field tests. For ethylbenzene and toluene, the higher rate constants for the field tests than for the lab tests could be the result of aerobic decomposition, which is very hard to avoid in field tests. On the other hand, the lower rate constants for the field tests as compared to the lab tests for trichloroethylene may be due to the fact that trichloroethylene degrades aerobically very slowly if at all (Bouwer, E.J. et al., Envir. Sci. & Tech. 15 596-599 [1981]). Exposure to air that might occur in field tests would not cause decomposition and would inhibit anaerobic processes, producing lower rate constants. The point to this extended discussion is that an in-depth examination of the assembled data could produce very helpful scientific information.

7) The screening procedure described in Section 2 greatly reduced the number of available studies from the numbers tabulated in the Syracuse report (it would be desirable to indicate the fraction of survivors that met the strict screening criteria). With all the work of screening to get this "elite" collection of data, it certainly is relevant to scrutinize the data (as noted in Item 6) and get out of it all that is possible.

8) The purpose of the screening was to get usable distribution of reaction rate constants for use in the EPACMTP model. The authors evidently are leaving it to someone else to decide whether the collection of data for each of the compounds listed provides a reasonable distribution of reaction rates. It is evident that the distribution is adequate for not more than a half-dozen of the compounds. Should not the authors make an assessment of the adequacy of the distributions (including their criteria for this assessment) ?

9) In Paragraph 2 of Section 2, the authors describe their selection procedure for screening out inappropriate results from the Syracuse report and any other new data. The procedure followed the prescriptions given in Appendix A. There is no information on biomass. There is no indication whether the samples were taken close in to the source of the plume (where the effective biomass might be expected to be higher, or far out in the plume where the concentration of nutrients and chemical of concern would be lower). The age of the exposure would be of help. Actually, this extra information is not needed for the EPACMTP model, so the authors cannot be faulted for not going beyond what is needed.

The EPACMTP model has the potential to do a good job of predicting what occurs at individual sites if it could use other parameters to adjust the rate constants. This kind of information could come out of the results of application of the EPA protocol discussed in Item 2 above. It might be desirable to apply the protocol to one of the chemicals of concern, such as benzene, to see if such rate constant could be adjusted to take account of the effect of type and nature of biomass, OR potential, and nutrient concentration. This, of course, cannot be done in the required framework of six months, but it should be a target for the future.

10) The great spread in results for the compounds is very interesting. In my opinion, it suggests that the protocol devised by EPA and described in the Federal Register (FR 53 No. 15, 22320-22323) is not the best approach for getting a distribution of rate constants, and that this random approach - getting data from a great variety of sites - may actually be better for giving a true picture of the variation in rates to be expected in the country. The protocol describes an excellent scheme for getting information on the fundamental biodegradation in the subsurface environment, and should be done at least in part. It is doubtful that the six sites chosen will provide enough information to get a population of reaction rates suitable for use in the EPACMTP model.

11) The serious problem of substances whose breakdown products are toxic and may degrade very slowly does not receive any attention. For some compounds this is not anticipated to be a problem, but it could be a very serious problem for chlorinated organic compounds. The literature probably gives enough information so that a user of any reaction rate distributions for the mother compound is made aware that a dangerous product may be formed. I believe the report should alert the reader to those compounds where a problem of this nature is likely.

12) Several of my problems with the report would not be problems if the authors had attempted to include objectives, discussion of results, conclusions and recommendations sections to their report. Why they would not include these sections mystifies me.

Minor problems

13) In Table F, a reference is needed for 1-methylnaphthalene (p F-41)

14) In Table E, < pH 6 is missing. Temperature is missing (p E-17)

15) The relationship of the chemicals examined in the report and presented in the tables to significant lists of toxic or hazardous compounds is not mentioned.

16) It is strange to see some of the compounds in the list. For example, acetic acid is listed, and there are no data satisfying the EPA protocol. Nevertheless, it is well known that acetic acid is easily degraded by methanogenic bacteria. The conversion of acetic acid to carbon dioxide and methane by methanogens is a principal pathway in the anaerobic digestion of complex wastes.

17) I found some inconsistencies between Table F and Tables D and E. For example, I noted the reference numbers in Table D and Table E and checked to see if they appeared in Table F (I believe they should appear in Table F since it is the sum of Tables D and E). I did this for benzene and toluene. For benzene, Reference 29 (methanogenic) is in Table E but it does not appear in Table F. Reference 19 (methanogenic) is in Table D but not in Table F. Reference 28 (methanogenic) is in Table F but not in either Table D or E. I found no problems with the tables for toluene. There may be a simple explanation for these inconsistencies, but it may be worth reviewing all of the tables for such glitches.

Response to Questions in "Charge to Review Panel"

18) Your Item C-1

I believe that using the EPACMTP model for its intended purpose is all right, and that first order rate constants are useful for this purpose. I am not sure about the use of the first order rate constants as calculated when there is a long latency period. The tabulated rate constants are for the rate after the latency period is over. It is likely that if the plume has reached some underground position and has been present for at least as long as the latency period, it should be all right to use the rate constants. That could be a substantial time after the site was producing leachate, because, as we know, the plume front advances slowly.

19) Your Item C-2

I do not have any new references/citations to suggest to add to the ones in the report.

20) Your Item C-3

I believe that the use of the first order biodegradation rates in the EPACMTP model is satisfactory for establishing the distribution of performances that is to be expected at the leaching sites in the country. This of course presumes that the model gets a correct distribution of reaction rates. In my opinion, of the 44 compounds listed in Table 2, there is enough information on perhaps a half-dozen of them for barely adequate distributions. There is a long way to go before there is any comprehensive answer for the numbers of toxic or hazardous compounds of concern.

21) Your Item C-4

I have addressed this issue in my Item 6 above. It appears that for some compounds the field data and the laboratory data can be merged without introducing substantial error, thus expanding the number of elements in the distribution. This may not be true in all cases. When the laboratory results are distributed in a higher range than the field test results (e.g., consider the case of trichloroethylene discussed above), I would give greater weight to the field results. It is reasonable to expect that field results will be less accurate than higher average rates than the laboratory results, but when results spread out over a 10 or 50-fold range, the differences in accuracy are dwarfed by other factors. Consequently, there is no strong reason to prefer lab results over field results.

If judgements are made as to whether field data, lab data or the combination of the two are closer to the truth, the distributions will be reasonable and can be used in the model. As noted earlier, the distributions will be very wide. The range of the predicted concentrations at some point in the plume will consequently also be very wide. They may be so wide that they are not of much value for the regulators or the regulated community. The distributions can be made more accurate and their range narrowed if other factors (probably the most significant are biomass type and density) could be included to adjust the rate constants. Possibly, nutrient concentration in the leaching liquid would be a correlating factor that would reduce the spread of the distributions. Of course, this would mean that an assessment of a site could not be made without this kind of information for the site.

B - 6

I do not believe that at this state of knowledge the EPACMTP model can be used to predict a specific outcome at a site unless an experimentally determined rate constant is available for that site.

22) Improvements that can be implemented within six months

I believe that most of the suggestions I have made can be implemented within 6 months. Obviously collection of new data cannot be completed in this time frame. In the long term, work should be supported directed towards including parameters in the model that will adjust the rate constants for the particular situations at the various sites.

Items that can and should be implemented within 6 months are:

* Item 1 - explain EPACMTP better.

* Items 2, 9, and 10 - These items support the conclusion that the approach suggested of developing distributions from existing and future data from field and lab studies, and not exclusively from data developed using the EPA protocol, is good. Continue on this path.

* Items 4 and 12 - The authors should expand the report and include objective, discussion of results, conclusions and recommendations. Many of the points I have raised would have been addressed if the authors took this standard approach to reporting results of an investigation.

* Items 6 and 11 - Critically analyze the data in the tables, draw conclusions and make recommendations on how to meld the lab and field data, and how to address toxic breakdown products. If the authors explain carefully how they came to their conclusions, others who use the report will be able to assess what they say and make their own judgements. Discussion by the authors of fine points and points the reader might overlook will improve the utility of the report.

* Item 5 - The authors should make Table 2.1 clearer. Standard deviation based on a normal distribution seems faulty. Even median and range (along with the number of observations - range requires that) would be better than standard deviation. The data should be looked at, such as in Figure 2. Looking at data is very useful.

* Items 7 and 8 - These items are related to Items 4 and 12. They must examine their data to properly complete Items 4 and 12.

* Items 13-17 - These minor items should be corrected.

* Item 18 - Experts familiar with application of the EPACMTP model should look into the implications of the latency period as it affects model results.

* Item 21 - The authors carefully assess the issue and should make recommendations on the best way to merge field and lab data.

ATTACHMENT C

**Peer Review of "Anaerobic Biodegradation Rates Of Organic
Chemicals In Saturated Zone" by:**

**David Yonge
Washington State University**

PEER REVIEW - ANAEROBIC BIODEGRADATION RATES OF ORGANIC CHEMICALS IN SATURATED ZONE

Reviewed by

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December 10, 1999

This report summarizes my findings regarding the review of the US EPA document entitled "Anaerobic biodegradation rates of organic chemicals in groundwater: A summary of field and laboratory studies for HWIR99" (hereafter referred to as EPAABR). In addition, the supporting documents, Syracuse Research Center report and 53 FR 22300, 40 CFR Section 795.54, were reviewed. My review summary covers the panelist questions and concludes with a general comment of the Syracuse Research Corporation Report.

Question 1: *Is the categorizing of rate data using the Monte Carlo technique as a substitute for data that is to be developed using the EPA's protocol published in the Federal Register adequate for the intended purpose?*

This approach to defining rate data for use in EPACMTP is appropriate for the intended purpose. The criteria for evaluating laboratory and field studies should yield rate data that is applicable for use in the predictive model. Furthermore, the selection of conservative (low) rate data affords a factor of safety and the Monte Carlo technique results in a statistically valid method of selection.

Question 2: *Are these rates for specific chemicals appropriate or are there other verifiable data available to supplement the data?*

For the chemicals I am familiar with, the rates are appropriate. Since the literature review responsible for the compilation of the rate data appears to have been concluded in 1997, I performed a "Current Contents" literature review to evaluate and update the rate data in the EPAABR report. This review covered the latter half of 1997 through 1999. Over 90 articles were recovered from the search query (search terms: "anaerobic biodegradation" and "leachate AND biodegradation".

After reviewing abstracts and reading selected articles, two articles were found to conform to the majority of the criteria for evaluating rate data (Appendix A and B of EPAABR) (Bradley and Chapelle, 1999; Bjerg, P.L., et al., 1999). The article authored by Bjerg et al., was particularly interesting since concentration-time data was collected in both laboratory batch and *in situ* microcosm experiments for five chemicals referenced in EPAABR. The *in situ* experiments were performed at different positions within a landfill leachate plume and the laboratory experiments were performed using soil and groundwater collected from within the plume. Temperature and redox potential was controlled to represent groundwater conditions in the laboratory experiments, abiotic controls were used in both experimental protocol, and the degradation experiments were carried out for up to 550 days (79 weeks).

Although first order rate constants were not presented in the article, the concentration - time data in the figures were adequate to estimate the first order rate constant, *k*, through application of Equation 1. Rate constants calculated in this manner are presented in Table 1 for toluene, m/p xylene, trichloroethene (TCE), perchloroethene (PCE), and ethylbenzene. These data indicate that, with the exception of TCE, data collected in a leachate plume environment, are within the

range of those reported in the EPAABR report. The TCE rate data are greater than the range of values reported in EPAABR, however, this would yield a conservative modeling result with regard to risk. Thus, the results of Bjerg, et al., validate the first order rate constants reported in the EPAABR report for the five chemicals evaluated.

$$k = \frac{\ln\left(\dfrac{S_0}{S_t}\right)}{\Delta t} \qquad (1)$$

where,
k = first order rate constant
S_0 = initial concentration
S_t = concentration at time t
Δt = time interval from S_0 to S_t

Table 1. First order kinetic rate constants from Bradley and Chapelle, 1999 and Bjerg, P.L., et al., 1999. Italicized values are from the EPAABR report.

Compound	Min (day^{-1})	Max (day^{-1})	Median (day^{-1})
Toluene	**0.018**	**0.041**	**0.039**
	0	0.186	0.02
m/p xylene			0.013
	0	0.17	0.0052
TCE[1]	**0.05**	**0.07**	**0.060**
	0.0082	0.04	0.0016
PCE[2]			0.071
	0	0.071	0.00186
Ethylbenzene	**0.00067**	**0.0035**	**0.0021**
	0	0.46	0.0031

[1] tricholoroethene
[2] perchloroethene

It is interesting to note that although toluene and PCE yielded relatively high first order rate constants following the initiation of degradation, they exhibited long lag periods (50 to 300 days for toluene and 100 days for PCE). This indicates the importance of carrying out degradation experiments for extended periods.

Question 3: *Is the use of a general first order rate expression appropriate for the intended use?*

Based on the intended use, the application of a standard first order rate term is completely appropriate. No less error would be incurred by attempting to use a Monod-based expression, as the simplifying assumptions made to describe the subsurface environment are likely to be the controlling factor in deviations of predicted from actual values (chemical concentrations).

Question 4: *Is laboratory data for use in the model an adequate substitute for field data?*

The use of carefully controlled laboratory experimental data is an appropriate substitute for field data. We have collected batch reactor (serum bottles) kinetic data in our laboratory to define anaerobic biological reduction rate constants for CrVI. The rate constants have then been applied in a modeling effort to design continuous flow column experiments. The model predictions were excellent. These and other results lead me to believe that the kinetic data are "transferable" to the field. The more significant challenge (and limiting factor) is in adequately defining the physical and chemical characteristics of the subsurface.

An error was noted on page 4 and 5 of the Syracuse Research Corporation report that involves the development of equation 4 and 6. Although a minor point, equation 3 should be expressed as

$$\frac{dS}{dt} = -k_0$$

instead of

$$\frac{dS}{dt} = k_0$$

Similarly, equation 5 should be expressed as

$$\frac{dS}{dt} = -k_1 S$$

To illustrate the need for the negative sign, integration and algebraic manipulation of the first order rate equation yields the following.

$$\int_{S_0}^{S_t} \frac{dS}{S} = -k_1 \int_0^t dt$$

$$\ln S_t - \ln S_0 = -k_1 t$$

$$\ln \frac{S_t}{S_0} = -k_1 t$$

or

$$\ln \frac{S_0}{S_t} = k_1 t$$

and

$$k_1 = \frac{\ln \dfrac{S_0}{S_t}}{t}$$

LITERATURE CITED

Bjerg, P.L., Rugge, K., Cortsen, J., Nielsen, P.H., Christensen, T.H., 1999. Degradation of aromatic and chlorinated aliphatic hydrocarbons in the anaerobic part of the Grinsted Landfill leachate plume: In situ microcosm and laboratory batch experiments, Ground Water, 37: (1) 113-121.

Bradley, P.M. and Chapelle, F.H., 1999. Methane as a product of chloroethene biodegradation under