UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

MAR 15 1983

OFFICE OF
THE ADMINISTRATOR

Dr. John W. Hernandez, Jr.
Acting Administrator
U.S. Environmental Protection Agency
401 M Street, S.W.
Washington, D.C. 20460

Dear Dr. Hernandez:

In May 1982, the Science Advisory Board (SAB) was asked to review the scientific and technical adequacy of the technical support data for the proposed effluent guidelines for the organic chemicals and plastics/synthetic fibers industry. The review, which was assigned to the SAB's Environmental Engineering Committee, has now been completed, and we are pleased to forward to you our report.

We appreciate the opportunity to work with the Effluent Guidelines Division on this interesting and challenging project. We know that the division is working to improve the quality of the analytical data base, and we expect to continue our review as the data base is updated and the statistical analyses are performed.

If you have any questions, or should you wish further action on our part, please call on us.

Sincerely,

Gerard A. Rohlich
Chairman, Environmental
Engineering Committee
Science Advisory Board

Earnest F. Gloyna
Chairman, Executive Committee
Science Advisory Board

cc: E. Eidsness
S. Schatzow
J. Denit
T. Yosie

REVIEW OF TECHNICAL SUPPORT DATA FOR THE PROPOSED EFFLUENT GUIDELINES FOR THE ORGANIC CHEMICALS AND PLASTICS/SYNTHETIC FIBERS INDUSTRIES

A REPORT

BY THE

ENVIRONMENTAL ENGINEERING COMMITTEE

SCIENCE ADVISORY BOARD

U. S. ENVIRONMENTAL PROTECTION AGENCY

February 1983

EPA NOTICE

This report has been written as a part of the activities of the Environmental Engineering Committee of the Science Advisory Board, a public advisory group providing primarily extramural scientific information to the Administrator and other officials of the Environmental Protection Agency. The Board is structured to provide a balanced expert assessment of the scientific matters related to problems facing the Agency. This report has not been reviewed for approval by the Agency, and hence its contents do not represent the views and policies of the Environmental Protection Agency, nor does mention of trade names or commerical products constitute endorsement or recommendation for use.

U.S. ENVIRONMENTAL PROTECTION AGENCY
SCIENCE ADVISORY BOARD

ENVIRONMENTAL ENGINEERING COMMITTEE

Dr. Gerard A. Rohlich (Chairman)
Professor of Environmental Engineering
and Professor of Public Affairs
Department of Civil Engineering
University of Texas at Austin
Austin, TX 78712

Mr. Harry C. Torno
Executive Secretary, EEC
U.S. Environmental Protection Agency
Science Advisory Board (A-101 M
Washington, D.C. 20460

MEMBERS

Mr. Richard A. Conway
Corporate Development Fellow
Union Carbide Corporation
P.O. Box 8361 (770/342)
South Charleston, WV 25303

Dr. Stanley N. Davis
Professor of Hydrology and Water Resources
Department of Hydrology and Water Resources
University of Arizona
Tucson, AZ 85721

Dr. Ben B. Ewing
Professor of Environmental Studies
Department of Civil Engineering and Institute for Environmental Studies
University of Illinois
408 S. Goodwin
Urbana, IL 61801

Dr. Davis L. Ford
Vice-President
Engineering Sciences, Inc.
3109 N. Interregional
Austin, TX 78722

Mr. George P. Green
Manager, Governmental Licensing
Public Service Company of Colorado
550 15th Street
Denver, CO 80202

Dr. J. William Haun
Vice-President, Engineering Policy
General Mills, Inc.
P. O. Box 1113
Minneapolis, MN 55440

Dr. George M. Hidy
General Manager
Environmental Research and Technology
2625 Towngate Road
Suite 360
Westlake Village, CA 92361

Dr. Raymond C. Loehr
Professor of Agricultural Engineering and Professor of Environmental Engineering
207 Riley-Robb Hall
Cornell University
Ithaca, NY 14853

Dr. Charles R. O'Melia
Professor of Environmental Engineering
Department of Geography and Environmental Engineering
The Johns Hopkins University
Baltimore, MD 21218

CONSULTANTS

ANALYTICAL METHODS

Dr. Russell F. Christman
Professor of Environmental Science
Department of Environmental Science
and Engineering
University of North Carolina
Chapel Hill, NC 27514

Dr. William Glaze
Head, Graduate Program in
Environmental Sciences
University of Texas at Dallas
Richardson, TX 75080

Dr. David Millington
Research Associate Professor
Department of Environmental Science
and Engineering
University of North Carolina
Chapel Hill, NC 27514

UNIT PROCESSES

Dr. Lyle F. Albright
Professor of Chemical Engineering
School of Chemical Engineering
Purdue University
West Lafayette, IN 47907

Dr. Michael R. Overcash
Professor of Chemical Engineering
North Carolina State University
School of Engineering
P.O. Box 5035
Raleigh, NC 27650

On May 25, 1982, the Environmental Engineering Committee (EEC) of the Environmental Protection Agency's Science Advisory Board was asked to consider four issues related to the technical support data proposed for use in setting effluent guidelines for the Organic Chemical and Plastics/Synthetic Fibers Industries. The four issues are:

1. Analytical Methods--Sampling, analytical methods, and statistical analysis of data.

2. Unit Processes--Systems by which the relationship between the occurrence and predictability of priority pollutants and the feedstock-generic chemical process combinations in use in the industry is established.

3. Estimation of Performance of Treatment Technologies using mathematical models.

4. Performance capability and effect of process variables on treatment technology for conventional and toxic pollutants.

In its approach to the problem, the EEC decided that issues 3 and 4 should be combined. Three subcommittees were formed to review the Contractor's Engineering Report[1] which had been submitted to the EPA's Effluent Guidelines Division: the Analytical Methods Subcommittee (Issue 1); the Unit Processes Subcommittee (Issue 2); and the Treatment Technology Subcommittee (Issues 3 and 4). The Analytical Methods Subcommittee and the Unit Processes Subcommittee were assisted by consultants. Comments were received from EPA, the Chemical Manufacturers' Association, and various attendees at Environmental Engineering Committee meetings and at subcommittee meetings.

This report summarizes the reports of the subcommittees and presents the conclusions and recommendations of the Environmental Engineering Committee. The full reports of the subcommittees and prepared statements submitted to the EEC are on file in the Science Advisory Board (SAB) offices. Minutes and verbatim transcripts of all meetings are on file in the Agency's Committee Management Office.

---

[1] Contractor's Engineering Report--Analysis of Organic Chemicals and Plastics/Synthetic Fibers Industries, Contract No. 68-01-6024, USEPA Effluent Guidelines Division, Washington, D.C., Nov. 16, 1981.

1. Analytical Methods Issue

The Committee reviewed the Contractor's Engineering Report and The Chemical Manufacturers' Association's CMA/EPA Five-Plant Study.

The data which were and are being used by EPA to develop the organics/plastics effluent guidelines can be divided into three general categories (phases). EPA and its contractors first collected data, using Gas Chromatograph-Mass Spectrometer (GC/MS) methods, in what was called the Screening Phase. The purpose of this phase was to identify, at a representative sample of industry facilities, the presence or absence of priority pollutants in the influent to and effluent from the wastewater treatment plants serving these facilities. Based on the results of the Screening Phase, the next, or Verification Phase, was designed to gather data using Gas Chromatograph/Conventional Detector (GC/CD) methods (with some GC/MS confirmation) both to verify the presence of pollutants detected in the Screening Phase and to quantify those pollutants. EPA concluded, before beginning the Verification Phase, that no adequately validated analytical methods existed for the industry, and therefore allowed the contractors actually doing the analysis to use "site-specific" methods (which were approved, however, by the Effluent Guidelines Division). The validity of the results from this Phase was to be assured by a Quality Assurance/Quality Control (QA/QC) program, also specified by the Effluent Guidelines Division. Data collected during the Verification Phase generally represented three or fewer days of operation at any of the sampled facilities. Subsequent to the Verification Phase, and because of reservations on the part of both EPA and the organics industry regarding the usefulness of the relatively short-term data collected, EPA, CMA, and five organic chemicals manufacturing plants initiated a study to develop a longer-term data base on the removal of priority pollutants by biological treatment systems. This study came to be known as the CMA/EPA Five-Plant Study, which, with the Screening Phase and Verification Phase, constitute the current data base that was reviewed by the Subcommittee and its consultants.

In its review, the Analytical Methods Subcommittee considered not only the analytical methods used, but also the statistical analyses to which these data were subjected and the way in which results were presented. In the case of the CMA/EPA Five-Plant Study, the Subcommittee also addressed certain engineering considerations.

Contractor's Engineering Report

Volume I and Appendices A-C of the Contractor's Engineering Report include results of the Screening and Verification Phases of the study to determine the distribution of priority pollutants in industrial wastewaters. The Subcommittee and the consultants reviewed the report and additional materials pertaining primarily to analytical and sampling methodologies used in the study. Based upon the review, the following findings and general conclusions are made:

a. The general plan, using an incremental approach and proceeding from Screening Phase to Verification Phase, was reasonable and necessary.

b. The execution of the plan may have been severely constrained by the decision to use GC/CD rather than GC/MS methods.

c. It is not possible to assess the validity of the data obtained in the Verification Phase because of the method of presentation used in the Contractor's Engineering Report.

d. The utility of the verification phase data (and other data available to EPA, but not in the Contractor's Engineering Report) may be improved by further analysis. It is also possible that, because of limitations built into the data such as the choice of analytical method or the quality assurance/quality control (QA/QC) methods applied, the data will have limited practical value.

e. Screening Phase data obtained using GC/MS methods are not included in the Contractor's Engineering Report and, therefore, could not be evaluated.

f. Verification Phase data are not presented in a useful format. Data for raw influents, treated effluents, and process water supplies are combined. Precision and accuracy are not calculated. It is recommended that the data be separated by sample type and then analyzed.

g. A statistical analysis of Verification Phase data is not included in the Contractor's Engineering Report.

h. Verification Phase data in the Contractor's Engineering Report were obtained by several contractors using several different analytical methods. It appears that EPA allowed contractors too much freedom in choosing analytical methods and in defining criteria for identifying compounds.

i. In light of present knowledge, the decision to use GC/CD methods in lieu of GC/MS in the Verification Phase does not seem justified. A limited number of GC/MS analyses to verify results were conducted in the Verification Phase, but the results are not in the Contractor's Engineering Report and have not been evaluated.

j. The procedures used for GC/CD analysis in the Verification Phase did not include confirmation normally used with these procedures.

k. All data obtained by industries during the Verification Phase are not included in the Contractor's Engineering Report and have not been evaluated. These data could be particularly useful if GC/MS methods were used.*

As a result of the SAB review, the Effluent Guidelines Division has undertaken work to upgrade the data base. They are establishing which data now in the data base are supportable, i.e., collected using valid methods including adequate quality assurance. They are also adding data into the data base, e.g., that collected by the plants under study and such confirmatory GC/MS data as was collected during the Verification Phase. Finally, they are separating, for precision and accuracy calculations, the influent and effluent data by pollutant. When these actions are complete, some of the criticisms noted above may be mitigated.

---

* Additional details may be found in the report of the consultants, on file in the SAB offices.

CMA/EPA Five-Plant Study

The Study, which resulted in a CMA report entitled CMA/EPA Five-Plant Study, was directed primarily at determining the ability of biological treatment systems to remove priority pollutants from industry wastewaters. In addition to the Study, the Committee and the consultants were provided with a detailed briefing by Study participants, including one of the Study's authors, on the contents of the Study and on additional analyses of the data done by Dr. George Stanko of Shell Development Company. Based upon this review, the following findings are presented:

a. Intralaboratory Precision--The Committee is particularly concerned with the manner in which intralaboratory precision was determined. Data from replicate analyses of a particular sample (taken at a certain plant on a certain date) by a single laboratory for a given organic compound were used to determine a standard deviation. Then, standard deviations for that compound from all laboratories (determined on samples from different plant sources and/or collected on different dates) were combined to determine "pooled" standard deviations. In a conventional sense, intralaboratory precision should have been determined by a large number of analyses of the same sample by the same laboratory. The "pooled" standard deviations, after being pooled again by pollutant groups (volatiles, acids, base neutrals), were used to determine reliability factors at 10-100 ppb levels. The resulting range of reliability was very broad (see Table 3.4 in the Five-Plant Study). Standard deviations determined for samples with concentrations largely below the practical detection limit of 10 ppb are used to calculate the expected variations of samples at concentrations levels of 100 ppb. We consider this extrapolation to be inappropriate. Confidence limits would be narrower if less pooling were done and if calculations were made in smaller concentration ranges, on a compound-by-compound basis, and for a single laboratory.

b. Interlaboratory Precision--The consultants consider that the authors of the CMA/EPA Five-Plant Study have underestimated the reliability of the data base. This arises from (1) the use of many measurements at concentrations less than 10 ppb, a practical lower limit for the reliable detection of volatile organics; (2) the pooling of data for several compounds into groups such as volatile organics; and (3) the use of all data including outliers. Perhaps using the phrase "interlaboratory reliability uncertainty" would be better than "pooled standard deviation."

c. Accuracy was determined using surrogate standards and fortified samples. Recoveries with these samples were highly variable. The data do not, however, answer the question of desirability of recovery corrections.

d. The large number of samples and replicate analyses ameliorate the impact of analytical imprecision on statements about pollutant removal in biological systems. The data base is fairly long-term (4-6 weeks), includes substantial GC/MS-derived components (66 percent of samples), and has adequate quality assurance (58 percent fortified samples, 32 percent spiked samples, and many split samples run by different laboratories). EPA has these data and should add them to the data base in the Contractor's Engineering Report.

e. "95 percent agreement" limits of concentration for each pollutant would be a valuable addition to the data base and to the establishment of effluent guidelines. (These could be determined in a manner similar to the 10 ppb limit for volatile organics described by Dr. George Stanko of Shell Development Company at the September 22, 1982 meeting of the Analytical Methods Subcommittee.)

f. Engineering Considerations--Since the Analytical Methods Subcommittee of the EEC was the only SAB group to review the Five-Plant Study, facets other than analytical were examined. Some points of particular interest are:

(1) The conclusion of "...toxic organic pollutants....are removed, with few exceptions, to or below the 10 ppb detection

limit....(by) biological treatment facilities installed to meet BPT ...." (see p. viii) should be qualified by these caveats:

a. Five classes of toxic compounds were excluded from the Study. Some of these may have been present at the plants.

b. The "few exceptions" above 10 ppb were, in fact, 16 out of 52 compounds, but 88 percent of the toxic compounds were below 50 ppb.

c. The treatment facilities evaluated rank in the top 45th percentile of all plants in terms of COD removal (p. 4-5). It should be noted that some less effective plants were included in the Verification Phase of the Contractor's study.

d. The effluent quality reflects not only biological treatment but also, in some cases, may include upstream physical/chemical steps.

(2) The report seems to support the conclusion that conventional (BOD) and/or nonconventional (COD) parameters cannot be used to indicate the presence or absence of priority pollutants.

(3) The results of the performance of the treatment systems focus on removal of pollutants. It is not known whether these substances are volatilized to the atmosphere, sorbed in the activated sludge, or biodegraded. It is important that the fate of these materials be established, but the Treatment Technology Subcommittee feels that airstripping is often overstated.

(4) The Five-Plant Study samples were collected during warm weather. The Five-Plant Study (pp. 7-2 and 7-3) indicates that similar results can be expected during cold weather periods, but data to substantiate this conclusion are needed.

As was the case with the Contractor's Engineering Report, the EPA's Effluent Guidelines Division, as a result of the SAB review, already is moving to upgrade the data base used in the Five-Plant Study. The Division plans to eliminate certain data due to analytical and poor-laboratory-practice considerations, to question and re-evaluate certain other data, and, as the only holder of the individual (unpooled) data from all sources, to perform improved precision and accuracy (confidence limits) calculations, including evaluations of inter- and intralaboratory variability.

Summary

The data as presently displayed and discussed in the Screening and Verification Phases of the Contractor's Engineering Report, are not amenable to interpretation with respect to their scientific adequacy. It is possible that by evaluation of all available data (reported and unreported), including statistical analyses, a scientifically adequate data base may be developed. It is also possible that the lack of GC/MS results and other factors may impair the use of the data for that purpose. All data obtained by industry and by EPA in the Screening and Verification Phases should be made available and should be evaluated. The data should be segregated by source (influent vs. effluent) and analyzed to determine precision and accuracy. The GC/CD data obtained in the Verification Phase should, where possible, be compared with GC/MS data.

The Five-Plant Study contains factors tending to provide a better data base. These include 4- to 6-week sampling periods, 66 percent GC/MS analyses, 58 percent fortified (spiked) samples, 32 percent replicates, and analyses of split samples by different laboratories. CMA's statistical analyses of the data in the Five-Plant Study, however, used questionable assumptions and procedures, and these may have produced conclusions about the analytical procedures which underestimate analytical reliability. The Five-Plant Study was designed with multiple objectives, only one of which was an evaluation of analytical reliability. This resulted in an experimental plan which apparently focused on treatability rather than on the determination of analytical precision, and which used debatable statistical procedures and analyses. Some specific findings were (1) that inter- and intralaboratory precision as defined in the Study (p. 3-2) was not truly determined and is not recoverable from the data; (2) that

the terms inter- and intralaboratory precision should be viewed as inter- or intralaboratory variation or uncertainty; and (3) that the concentration for each pollutant that would give "95 percent agreement" should be established.

This review of the scientific validity of the analytical data base for the development of effluent guidelines for the organic chemicals and plastics/synthetic fibers industries by the EEC has had the favorable impact of identifying certain additional work that can be done readily to improve the data base. Such work has been initiated by the Effluent Guidelines Division. We believe that future work should have continuing peer review. EPA may also wish to ask the EEC and its consultants to review any significant new findings.

2. Unit Processes Issue

The following findings are based on the Unit Processes Subcommittee's review of Volume III of the Contractor's Engineering Report. Volume III describes the system by which the relationship between the occurrence and the predictability of priority pollutants, and the feedstock-generic chemical process combinations in use in the industry is established.

a. We believe that the generic product/process approach described in Volume III is conceptually sound and can be developed into a tool to qualitatively predict the occurrence of priority pollutants in raw wastewaters, with the following reservations.

1. The method has been applied, thus far, to only a small portion of the organics industry.

2. The Committee has no evidence that a data base is currently available to enlarge the coverage substantially.

3. The method is not likely, in the foreseeable future, to be adequate for quantitative determinations of the presence of priority pollutants in plant wastewaters.

b. A thorough error-checking of Volume III should be done. There are numerous minor errors in the description of product/processes.

c. A complete set of references should be developed and included in the document, particularly where conclusions are based upon information in the literature.

d. The effects of the uncertainties should be addressed. Among these are the possible presence of contaminants in water supplies and in raw materials, and the uncertainties arising from reactions among wastewater components after mixing.

e. The data base should be expanded to cover a broader range of products/processes.

f. There should be some evaluation in Volume III of how well the system could be expected to perform (for instance, by applying the method to plants where data are available).

g. Development of this system may be essential as a predictive tool for new source discharges.

h. Volume III should be subjected to on-going peer review as revisions or additions are made.

i. Volume III, in its present form, is not technically adequate for making quantitative determinations of the presence of priority pollutants in plant wastewaters.

j. The system will be best used to provide relative rankings of the possibility of pollutant discharges, rather than to establish absolute discharge levels.

Based upon these findings, the Committee concludes that the system, as described, has merit and should be further developed.

3. Treatment Technology Issue.

This section is based upon the review of Volumes I, III, IV, and V, and Appendices A, B, C, and L of the Contractor's Engineering Report.

The overall objective of the documents was to determine what constitutes Best Available Technology Economically Achievable (BAT) for the organic chemicals and plastics/synthetic fibers industries so that effluent guidelines can be promulgated under provisions of the Clean Water Act. The overall approach was to develop computer models which will select a feasible waste treatment process train for various treatment levels, size treatment units, and determine the capital and operating costs. Ultimately, the objective is to develop the relationship between effluent levels and cost.

The Committee was asked to (a) review the process models developed by the EPA contractors, (b) comment on the representativeness of the process variables and validity of the models compared to actual treatment systems, and (c) review selection rules and technology levels for combinations of individual processes. The Committee was also asked to evaluate the applicability of these processes, the validity of the ranges of operating and design variables, and the representativeness of the treatment trains in industrial use. However, in order to properly assess models and evaluate the representativeness of the variables, it would have been necessary for the EEC members to become intimately familiar with the models through hands-on use. The Committee had neither the time nor the opportunity to do so.

The following comments and observations are based upon the review.

The great variety of feed stocks, processes, and products in the industries, the highly variable composition of raw wastes produced by these complex systems, the variety of waste treatment processes which may be used (many of which are affected by numerous process variables), and the difficulties of identifying and quantitatively measuring trace organics in very complex mixtures make the task of developing effluent guidelines very difficult. Many compromises were clearly necessary, and the outcome of modeling for establishing costs will be affected by these compromises.

Raw Waste Loads

The generic methodology used to predict the presence or absence of priority pollutants in industry effluents presented in the contractor's document is logical. The Committee is concerned about the model input information, however. The reliability of raw waste load projections should be better documented. Experience indicates that the raw waste load probably varies substantially for any given plant.

One of the compromises used was to base raw waste loads on data from relatively few chemical plants and for short sampling periods. The 308 survey generated data from 566 plants. The Screening Phase of effluent and influent sampling was based upon 40 plants. The Verification Phase for those 40 plants utilized a three-day sampling period. These provide the input data for establishing raw waste loads for the models. The only long-term sampling data, which can be used to partially verify the raw waste loads and establish their representativeness, is from five plants. There is little evidence in the reports to support the assumption that representative raw waste loads can be based upon a three-day sampling (as in the Verification Phase) or on a longer-term sampling of only five plants. The entire project is dependent upon a data base that was evolutionary in its initial years with respect to methodology and QA/QC. The pre-1979 data need to be validated or up-graded.

While the precision and accuracy of the analytical methods for priority pollutants are not well established, it appears that concentrations of priority pollutants in any single sample might be within a 95 percent confidence of about 5x the correct values. However, as stated in the Analytical Methods Issue sections of this report, this estimate of confidence may become narrower when all available data are considered and properly evaluated. After consideration of representativeness of samples during the short sampling period, the Committee concluded that the presently reported data on priority pollutant concentration has a reliability of less than an order of magnitude. The precision is poorest at the low concentrations found in the effluent.

Biological Treatment

Treatability studies were conducted for biological treatment processes, activated carbon, steam stripping, organic adsorption resins, and metals removal by precipitation or ion exchange.

The major organic chemical waste treatment technologies are biological treatment processes, such as activated sludge, trickling filters, and aerated lagoons. Biological systems for high concentrations of organics can be enhanced measurably by pre- and/or primary treatment to remove materials that would adversely affect the biological system. The designers of the overall design logic used in the models recognized the importance of pretreatment or primary treatment and built the model to signal for pretreatment when the influent is characterized to exceed preset levels of certain constituents. It is not clear that the model will go back and look at in-plant controls or pretreatment of individual waste streams prior to combination in a single plant raw waste stream.

Multimedia models for biological treatment are discussed in the documents. The relationship of the detailed discussion of these models to the approach used for effluent prediction and cost estimates is not clear. Much of the discussion of the models in Volume I appears to be irrelevant to their final use. As such, the discussion of the models tends to confuse, rather than clarify, the logic and approach that was used.

In addition, several of the models appear to include questionable assumptions or constants. For example, the Hwang model, shown in Volume I, Figure 3-6, includes a component for air stripping, using rate constants determined experimentally or from the combination of the individual liquid and gas phase gas transfer constants. It is quite probable that this approach significantly over-predicts the air stripping component. Evaluation of air stripping of hydrocarbons in a petrochemical wastewater[2] showed that the air-stripping equation, which did not account for removal of all of the organic compounds by biological processes, over-predicted total hydrocarbon concentration by a factor of 45-150 times. The statement in the Conclusions section that multimedia models need to reflect the recognition that air

---

[2] Engineering-Science, Inc., Evaluation of the Potential for Air Stripping of Hydrocarbons During Activated Sludge Treatment, Prepared for the Industrial Advisory Council, Washburn Tunnel Plant of the Gulf Coast Waste Disposal Authority, March 1979.

stripping is a factor may, in fact, be overstated for many priority pollutants. Air stripping is not taken into account at all in the computer models as they are currently developed. This is appropriate, although it leaves the reader confused about the reason for the detailed discussion of the Hwang model, which includes a component for air stripping.

The various predictive models are adequately discussed in the contractor's document. Moreover, the basis for determining the biodegradability of selected priority pollutants used in the Catalytic Second Phase Study, as well as in the Oklahoma State University study, is clearly described. It should be noted, however, that the impact of antagonistic or synergistic effects of other compounds in solution on the biodegradability of selected constituents is difficult to quantify, and may be substantially different from observed kinetics of single or controlled substrates. Therefore, in any complex chemical industry, particularly in specialty chemical facilities, one could expect variation in the level of biodegradability of selected priority pollutants. This is underscored by the variability of priority pollutant degradability, as previously published by EPA. The priority pollutants monitored through these biological treatment systems in the CMA/EPA Five-Plant Study indicated effluent quantities in the range of 100 ppb or less[3]. The process variables which affect the exact biodegradability, such as temperature, pH, TDS, and presence of other organic and inorganic constituents in solution, are not included in these models and must be determined empirically. Again, due to the complexity of the industry, model verification is difficult unless these variables and their influence on the level of treatment is ascertained.

Temperature is probably the most significant variable affecting the biological treatment of the industry's wastewaters. Temperature is not a great problem for municipal wastes and the less complex industrial wastes, such as food processing or refinery wastes, if the plant is properly designed for the range of temperatures encountered. Experience has shown,

---

3 Chemical Manufacturers Association, CMA/EPA Five-Plant Study, Engineering-Science, Inc., March 1982.

however, that temperature is a highly significant factor in determining the removal of the complex organic compounds found in the organic chemicals, plastics and synthetic fibers industry wastes. Normally, the more complex and water soluble a constituent is, the more pronounced the temperature effect on its biodegradability[4]. This is attributable to the effect of the molecular energy of activation incorporated into the accepted temperature equations. The conclusion in the report that "temperature had little effect on design because of the safety factor" does not appear to be supported by experience in this industry. Moreover, the question arises whether or not the costs involved in control of temperature by adding steam or heat to the system have been factored into the overall cost analysis. The computer model apparently checks influent temperature with a specific activated sludge influent temperature subroutine which, if the temperature is less than 50°F or greater than 100°F, adjusts the temperature via steam injectors or heat exchangers. Presumably the cost of steam injection or heat exchange is included.

Another question revolves around the stated COD/BOD ratio of 3.0 and TOC/BOD ratio of 1.25 being used as a computer input to the biological models. This ratio has been shown to vary widely within the organic chemicals industry and would likely have a significant effect on the "K" rate of the models presented in Volume I. It could be postulated, for example, that an inverse relationship exists between the COD/BOD ratio and the "K" rate. In the report, K values for biological treatment are based upon concentrations less than the detection limit. The basis for this needs to be justified. The model should be constrained to the detection limit for input and output data.

Because of the effect of these various process variables, especially temperature, biological treatment process models are of limited use in establishing the effluent concentration of priority pollutants. If they are to be used for this purpose,

---

4 Gloyna, E. F. and Ford, D. L., "Establishing a Basis for the Design of Industrial Wastewater Plants," 1976.

justification needs to be provided and the logic made explicitly clear. If models are to be used to size units in a treatment train and estimate costs, but not used to estimate effluent concentration of priority pollutants, then the point needs to be made clear, and the basis for determining priority pollutant effluent concentration needs to be fully described.

Activated Carbon Adsorption

Many refractory organics are amenable to treatment by activated carbon. There are already about 100 large scale plants in use for this purpose. However, the information or statistics upon which the activated carbon "model" is based (pg. 3-62) use extrapolation from laboratory results. It would have been more appropriate for EPA to engage in a comprehensive sampling program of some of the 100 large scale plants and base the use of activated carbon on the results of that program. Both equilibrium and dynamic carbon testing, as well as some full-scale plant information, were used to predict the effect of activated carbon in removing priority pollutants. Isotherm techniques can be used as "screening" testing only and cannot be used as a basis for extrapolating actual priority pollutant removal in multicomponent wastewaters[5]. The dynamic mini-column adsorption technique (DMCAT) is stated as being capable of rapidly generating necessary design data to assess the performance of an adsorption system for single and multicomponent waste streams. This statement is not substantiated and needs to be referenced or supported. Table 3-14 cites the performance of full-scale systems in removing priority pollutants. It should be noted that there is signficant variation in the stated percent removals of the same constituent. This is understandable, as there are many variables which enter into the precise adsorption efficiency of given constituents. These include, but are not limited to, the interactive effects of other constituents present in multicomponent systems on the sorption/desorption phenomenon, temperature and pH, the location of exact functional groups on given constituents, the molecular configuration of these constituents, their polarity, their water solubility, and

[5] Perrich, J. N., Activated Carbon Adsorption for Wastewater Treatment, CRC Press, Boca Raton, Florida, 1981.

many other process variables which will affect the exact adsorption of these constituents. These variables are well understood by most investigators, and it is virtually impossible to develop truly representative models or to extrapolate observed plant performance to other plants relative to the precise adsorbability of priority pollutants. For these reasons, both equilibrium and dynamic models often over-predict the effectiveness of activated carbon in adsorption removal. Moveover, interference by inorganic and organic substances in complex wastewaters will distort the ability of going from bench and pilot-scale studies when establishing a basis for predicting full-scale performance. Effects of these process variables have been published previously. In summary, models using laboratory or pilot scale adsorption data cannot be used to predict accurately the performance of full scale activated carbon adsorption processes. A much better approach would be to base performance prediction on some of the full-scale plants which exist in the U.S. and abroad, including plants in the petrochemical industry. The documents provided no information on why this was not done.

In addition to the comments above on the two major processes, the Committee notes that the list of treatment catalog unit processes presented in the Contractor's Report, Volume I, Table 3-35, page 3-185, appears to be an unusual grouping of processes. It is not clear how it was generated, or how it is to be used.

The use of solvent extraction may be questionable as a treatment process for large volumes of wastewater. Loss of solvent in small amounts can add dramatically to costs. EPA should re-evaluate this suggestion.

Cost Estimates

The capital and operating cost information developed by the contractor is not included in Volume I. The basis for developing this information, however, is described. All costs are in 1977 dollars (pg. 3-247). These costs should be suitably upgraded and should include such factors as the Marshall and Swift Index, the Engineering News-Record Index (ENR), the Large-City EPA Index, and the Small-City EPA Index. The chemical industry is clustered in selected parts of the United States, and other factors, such as geographical location or land availability, may be important. For example, the fraction of the national average construction costs for various areas within the country range from .74 in the Southwest to 1.15 in the Midwest and East[6]. These factors can distort the costs significantly. In Volume I, Figure 3-13 to 3-20, a comparison of the costs generated by the model with those of real plants was presented. A review of these plots raises some questions as to degree of correlation. As a minimum, correlation coefficients should have been established to quantify the verification of the contractor's cost models. It is possible that some of the factors which significantly affect both capital and operating costs were incorporated into these costs curves and simply were not mentioned in the contractor's document. It is not possible to determine this in a direct review of the report. EPA should be prepared to defend these costs with more backup information than that included in Volume I.

Verification

There is little information about model verification. There needs to be reconciliation of the process effectiveness of the nonbiological methods, cited by EPA in Volume I, with the levels of treatment presented by CMA in the Five-Plant Study. The effluent concentrations of BPT/BAT models in the contractor's report should be reconciled with those averages actually attainable and practiced by exemplary plants.

The degree to which analytical precision and accuracy limit the measurement of either the raw waste load or the effluent concentration is still unknown, since available data have not been effectively analyzed. The Effluent Guidelines Division is now doing this. The additional uncertainties in treatment plant performance mean that the effluent concentration for priority pollutants cannot be predicted by the models with any certainty. Also, the limited "Benchmark Analysis," comparing real costs with costs predicted by the model (figure

6 American Petroleum Institute, Economics of Refinery Wastewater Treatment, API Publication No. 4199, August 1973.

3-13 through 3-20), appears to reflect variations of 2x to 5x. The "Benchmark Analysis" was an attempt to compare the modeling approach with real plant information and process performance. The comparison noted important differences in effluent concentrations and treatment system costs. These differences cannot be ignored or attributed to simplistic rationalizations. More comparisons between model and real world results, as well as better relationships, are needed before any defensible comparison between the EPA approach and real performance and costs can be established. The Committee encourages EPA to obtain a better understanding of why there are such signficant differences and to modify the EPA approach to better reflect actual effluent concentrations, treatment plant performance, and costs. The model appears to predict a "lower limit" on capital costs. Given, then, that the resulting cost vs. effluent quality relationship is not a sharply defined curve but rather a very broad band, it will be difficult for decisions to be made as to what constitutes the Best Available Technology Economically Achievable.

Current knowledge of the fate and transport of priority pollutants and of either ecological effects or health effects is not adequate for any reliable benefit analysis of regulations for their control. Interpretation of the level of treatment which constitutes Best Available Technology Economically Achievable will depend greatly upon its economic impact on the affected industries and/or the consuming public.

There are many pages describing potential models and considerable data describing research results in the report; it was not obvious how EPA planned to use the models or the data to reach decisions. It would be desirable if the EPA documents would include a simple discussion, including, perhaps, a step-by-step flow diagram, of what will be done to reach a particular conclusion regarding appropriate treatment technologies and levels of treatment. If possible, examples using a biotreatment process and a non-biological process should be included.

Summary

The concept used by the EPA contractor is logical, although little information on the data base variability is available. The computerized modeling system, designed to evaluate the end-of-pipe system and in-plant controls, is subject to the accuracy and applicability of the computer file input. This model input data should be carefully evaluated and justified.

There is a large degree of uncertainty, both in the reliability of the laboratory analyses for priority pollutants and in the representativeness of the samples taken over short periods and for few plants.

Biological treatment process models do consider the effect of temperature on treatment effectiveness and on cost. More confirmation and verification of the models by comparison with actual full-scale biological process treatment plants is needed.

Activated carbon adsorption models should be verified with actual operating data from full-scale treatment plants and not from laboratory or pilot plant data.

The Committee strongly endorses the concept of pretreatment or primary treatment. The use of biological treatment processes is the most common approach to treatment of mixed waste streams. The models should make clear that physical and chemical processes will be used to treat organic chemical industry wastewaters and will usually be applied upstream of the biological process. This pretreatment will often be most economically applied to individual process waste streams.

The statement in the "Conclusions" section of the discussion of biological treatment (p. 3-86, Vol. I) that multimedia models need to reflect air stripping may, in fact, be overstated. Apparently the computer models for plant sizing and cost determination properly do not consider air stripping.

Further verification of the models for predicting cost of treatment trains designed for various effluent quality levels is needed. Experience indicating the use of models for design and costing of Publicly Owned Treatment Works (POTWs) may be helpful in verifying their applicability to organic chemical industry wastewaters.

4. Summary And Conclusions.

The Environmental Engineering Committee (EEC) of EPA's Science Advisory Board (SAB) has reviewed the technical support data proposed for use in setting effluent guidelines for the Organic Chemical and Plastics/Synthetic Fibers Industries. Detailed analyses of the Contractor's Engineering Reports are presented elsewhere in this EEC report. Based upon our review, the following summary statements and conclusions are made.

Analytical Methods

1. The data from the Screening and Verification Phases of the Contractor's report are not amenable in their present form to interpretation with respect to their scientific adequacy. The Effluent Guidelines Division has agreed to reanalyze the data.

2. The CMA/EPA Five-Plant Study provides a better data base than that of the Contractor's report. The statistical analyses in the Study use questionable assumptions and procedures, which may produce conclusions which underestimate analytical reliability.

3. It is possible that by evaluation of all available data from the two studies (reported and unreported), including statistical analysis, a scientifically adequate data base may be developed.

Generic Products/Processes

4. The generic product/process approach is conceptually sound, but the Committee has the following reservations with regard to its use to predict the occurrence of priority pollutants in raw wastewaters:

a) The method, thus far, has been applied to only a small portion of the industry;

b) There is no evidence that a data base is available to enlarge the coverage; and

c) The method is not adequate for quantitative determinations of priority pollutants.

5. The effects of uncertainties, such as contaminants in water supplies, in raw materials, and those arising from reactions among wastewater components, should be considered.

6. The generic product-process approach, in its present form, is not technically adequate for making quantitative determinations of the presence of priority pollutants in plant wastewaters.

7. The system can be used to provide relative rankings of the possibility of pollutant discharges rather than to establish absolute discharge levels.

8. The generic process/products system has merit and should be further developed.

Treatment Technology

9. The concept used is logical, but little information on the variability of the data base is available.

10. There is a large degree of uncertainty both in the reliability of the laboratory analyses for priority pollutants and in the representativeness of samples taken over short periods and for few plants.

11. Biological treatment process models should consider the effect of temperature on treatment effectiveness. More confirmation and verification of the models by comparison with full-scale biological treatment plants is needed.

12. Activated carbon adsorption models should be verified with operating data from full-scale treatment plants.

13. Further verification of the models to predict cost of treatment trains designed for various effluent quality levels is needed.

14. The selection of effluent concentrations which reflect best available technology economically achievable is based upon a cost vs. effluent concentration relationship. It must be recognized that this relationship will not be sharply defined, but broad band. Neither the costs nor the effluent concentrations can be precisely determined by modeling methods.

7. The system can be used to provide relative rankings of the possibility of pollutant discharges rather than to establish absolute discharge levels.

8. The generic process/products system has merit and should be further developed.

Treatment Technology

9. The concept used is logical, but little information on the variability of the data base is available.

10. There is a large degree of uncertainty both in the reliability of the laboratory analyses for priority pollutants and in the representativeness of samples taken over short periods and for few plants.

11. Biological treatment process models should consider the effect of temperature on treatment effectiveness. More confirmation and verification of the models by comparison with full-scale biological treatment plants is needed.

12. Activated carbon adsorption models should be verified with operating data from full-scale treatment plants.

13. Further verification of the models to predict cost of treatment trains designed for various effluent quality levels is needed.

14. The selection of effluent concentrations which reflect best available technology economically achievable is based upon a cost vs. effluent concentration relationship. It must be recognized that this relationship will not be sharply defined, but broad band. Neither the costs nor the effluent concentrations can be precisely determined by modeling methods.