

Environment

PPG Industries, Inc. Chemicals P.O. Box 1000 Lake Charles, Louisiana 70602

W. J. Peard
Manager
Laboratory Services/Environmental

July 25, 1988

Ms. Maureen O'Neill
Assistant Secretary
Office of Water Resources
Department of Environmental Quality
P.O. Box 44091
Baton Rouge, LA 70804

Re: Comments on the Proposed 1988 Triennial Revision of the
Louisiana Water Quality Standards (First Draft)

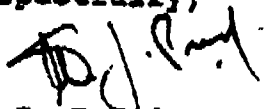
Dear Ms. O'Neill:

Attached are the subject comments of PPG Industries Chemicals Group Lake Charles Works. We appreciate the opportunity to comment on this important document and to work with your staff in developing realistic and attainable water quality standards for Louisiana surface waters.

Our comments include general comments related to the overall standards-setting approach taken by DEQ, as well as some site-specific comments relating to the Calcasieu River System, and including PPG's receiving waters.

Thank you for the opportunity to comment on the Proposed Louisiana Water Quality Standards, and PPG hopes that DEQ will give our comments serious consideration.

Respectfully,


W. J. Peard
Manager, Laboratory Services/
Environmental Control

Attachment

CERTIFIED MAIL (P 691 563 329)

bcc: E. McHam, EPA Region VI
LCA
Calcasieu Tech. Water Committee
W. Graybill/R. Samelson/A. Tolmsoff
J. Wyche/M. Wood/J. Rusnak
File #301.2.08

SL 106241

PPG Industries, Inc.
Lake Charles, LA
Comments

A. Scientific Advisory Committee

The proposed standards should authorize and establish a Scientific Advisory Committee to advise Louisiana DEQ staff on technical matters relating to Water Quality Standards development and updating. The committee should be composed of qualified, reputable toxicologists, chemists, hydrologists, and other scientists from government, academia, and industry. Duties of the committee should include advising and developing recommendations regarding the following issues as they relate to the Water Quality Standards development process:

Toxicology (mammalian and aquatic)
Chemistry (analytic and aquatic)
Hydrology and Hydrodynamic Modelling
Chemical Engineering Processes

These are all highly technical areas where DEQ staff and the standard setting process could benefit from outside guidance and assistance. For example, for this and future triennial reviews, the Committee would make recommendations on what additional chemicals warrant regulation as carcinogen suspects, and at what risk level the numerical criteria should be established.

B. Range of Options Available

Louisiana DEQ has considerable latitude within the Water Quality Standards development process, and is not required to adopt all of the EPA-recommended criteria and advisories for toxic pollutants. They are intended only as guidance documents to help states in their standards-setting process. The approaches and procedures taken by other states (e.g. Michigan, Ohio, Texas) should be examined to gain the benefits of their experience.

C. Non-Applicability to Groundwater

There are apparently conflicting statements in the Introduction of Section 1101 which need to be resolved. In the last paragraph of Page 1, the statement is made that "The water Quality Standards described in this document . . . do not apply to effluents or ground waters." At the top of page 2, the paragraph goes on to state that "The standards . . . may be subsequently used for protection of groundwater." These statements should be clarified.

SL 106242

D. "Use Attainability Analysis" Clarification Needed

On page 5, the definition of "Use attainability analysis" needs to be expanded and clarified. After reading Section 1109.-Policy, and especially Sections 1109.C.1.d regarding Policy exceptions for Intermittent Streams, and 1109.C.2.c regarding Policy exceptions for man-made water courses, the reader is left with an appreciation that this is a potentially very important means of exempting certain surface waters from standards applicability, but is left without a clear understanding of how the use attainability analysis is to be performed or what the important variables will be in deciding whether a stream is exempted.

E. "Reasonableness" of Proposed Standards is Questioned

On page 14, under Section 1109.F.1-"Water Quality Standards Revision Process", the statement is made that:

It is the position of the state of Louisiana that the standards contained herein are those that are reasonable on the basis of the present or potential quality of our waters, present and future water uses, and the best practicable wastewater treatment under any conditions.

PPG strongly disagrees with this statement, and in particular, reasonableness based on the best practicable wastewater treatment. It is PPG's opinion that DEQ reached that conclusion at least in part, based on information presented by Walden and Bostock in their LSU report entitled Calcasieu River: A Louisiana Toxics Problem. The report presents results of a feasibility evaluation by mathematically modeling Bayou D'Inde, Bayou Verdine, and the Calcasieu River. Following calibration of the model with actual measured wasteloads and ambient water quality data, predictions of future ambient VOC concentrations were made. This was done by adjusting PPG's wasteload of specific VOCs to conform with those resulting from application of specified BAT Effluent Limitation Guideline values for the OCPSF Industry. The resulting output indicated that all VOCs with the exception of chloroform, would be in compliance with the proposed Louisiana numerical criteria.

The assumption that the BAT levels for VOCs are attainable with the identified BAT control technology (i.e. Steam Stripping) is incorrect. For OCPSF Facilities where end-of-pipe biological treatment would not be effective (biological treatment will not work on chloroorganics), the BAT values for VOC are based on data from only two plants. PPG's Lake Charles facility was one of those plants. Both plants have challenged the attainability of the BAT limits in a suit filed in the Fifth Circuit Court of Appeals.

SL 106243

To assume that these values are attainable by the identified BAT control technology for VOCs should be premature for DEQ and in PPG's opinion, incorrect.

F. Analytical Detectability/Specificity

Water Quality Standards should not be set at concentrations which are at or below the Method Detection Limit (MDL) for EPA-approved methods which have been developed and validated with intra- and inter-laboratory studies (e.g., USEPA Methods 624-625 or the 601-612 series) for organic priority pollutants. The numerical criteria that have been proposed for many toxic organic pollutants on pp 28-29 are below their MDL's for the 624 and 625 methods. They are especially far below the MDL for benzidine, hexachlorobenzene, PCBs, 1,1-dichloroethylene, chloroform, and other trihalomethanes. Inasmuch as the MDLs were established with a reagent water matrix, it should be realized that the actual water sample matrix is more complex. This would raise the detection limits substantially, making the concentrations even more difficult to measure.

At the limit of detection (LOD), an analyst can only say whether or not a compound is present, not at what concentration. The American Chemical Society (ACS) defines LOD as the "lowest concentration level that can be determined to be statistically different from a blank". ACS recommends that the "limit of detection" be three times the standard deviation of the background noise level. Not until the LOQ (limit of quantitation) concentration is reached can one begin to reliably measure the amount of the compound. ACS recommends that the LOQ be at least ten times the standard deviation of the background noise level. For instance, given that the LOD is 10 ppb (based on the Method 624 minimum levels), the LOQ would be at least 33 ppb. In practical terms, then, the analyst cannot reliably determine that the system is not in compliance until a concentration level of at least 33 ppb is present.

The 1983 ACS publication, "Principles of Environmental Analyses", has further comments on low-level measurement:

Data measured at or near the limit of detection have two problems. The uncertainty can approach and even equal the reported value. Furthermore, confirmation of the species reported is virtually impossible; hence the identification must depend solely on the selectivity of the methodology and knowledge of absence of possible interferents. These problems diminish when measurable amounts of analytes are present. Accordingly, quantitative interpretation, decision-making, and regulatory actions should be limited to data at or above the limit of quantitation.

SL 10624-

The analytical results in the CMA/EPA 5-Plant Study and an EPA Round-Robin lab study show that analytical uncertainty at even the 10 ppb level is so high that laboratories cannot agree reliably on the presence or absence of a pollutant. This will be even more pronounced if detection will be required at <1 ppb.

Even the 10 ppb "limit of detection" is applicable only to low interference samples. At the low concentrations of analytes proposed on pp 28-29, considering the analytical variability, uncertainty, and sensitivity of the methodologies, data submitted for model validation would be highly subject to false positives as well as questionable quantification.

G. Water Use Designation

The use designations are not realistic if the goal is to turn even dredged drainage ditches into fishable/swimmable water bodies. PPG believes the designations should instead reflect actual use, or reasonably probable future use. The definition of "Primary Contact Recreation" on page 16 under Section 1111-"Water Use Designations" needs to have realistic assumptions factored into it. For example, it is unreasonable to expect that individuals would swim, water-ski, or scuba-dive every day of their lives, and that they would accidentally ingest two liters of water each day. Nevertheless, when DEQ applies EPA-recommended criteria for the protection of human health by the ingestion of contaminated water and contaminated aquatic life to a stream section which lacks a "Public Water Supply" designated use, those are the implied assumptions, since EPA based these on a daily intake of 2.0 L/day over a 70-year life span.

H. Criteria

1. Site-Specific Criteria should be Authorized. The brief discussion of this issue on page 17 under Section 1113-"Criteria" needs to be expanded to make it clear that criteria can (and indeed ideally should) be based on site-specific background water quality conditions, and based on studies performed on relevant locally-indigenous species. For example, criteria derived from tests using cold-water species in non-saline, soft-waters are inappropriate for establishing standards for protection of warm-water species in tidal-influenced waters of Louisiana.

2. A Combination of Narrative and Numerical Criteria is Preferred. Louisiana should follow the precedent of other environmentally responsible states such as Michigan, Ohio and Texas which have developed standards for a selected number of pollutants consisting of a combination of narrative and numerical criteria. PPG believes it is inappropriate for Louisiana to develop specific numerical criteria for a long list of toxic pollutants.

SL 106245

3. Chloride Criteria. The chloride criteria on pp. 22-23 need to be revised to conform with EPA's February, 1988 final report entitled Ambient Water Quality Criteria for Chloride - 1988 (EPA 440/5-88-001).

4. Toxic Substances Criteria.

a) "Red Book" Criteria Should Not be Used. On pag 26, the statement is made under Section 1113.B.6.-"Toxic Substances" that numerical criteria for specific toxic substances are "mostly received from EPA publications, including: (1) 1976. Quality Criteria for Water (commonly referred to as the "Red Book"), and others, including the "Gold Book". CMA, other trade associations, and individual companies have extensively commented on the "Red Book" and it has been discredited as a responsible source of guidance to states. PPG feels very strongly that this document has no place in the establishment of enforceable and responsible ambient water quality standards.

b) Use the Best and Most-Recent Data in Setting Numerical Criteria. The numerical criteria for trichloroethylene on page 28 include criteria for the protection of fresh water and marine aquatic life, and are apparently based on the recommended "Gold Book" Criteria. It should be noted that the "Gold Book" based its acute toxicity criteria for saltwater aquatic life on a behavioral end point (i.e. signs of intoxication) rather than a 50% mortality end point which defines LC_{50} . Furthermore, that end point was based on a higher test temperature, and use of a carrier solution (triethylene glycol) to introduce the trichloroethylene into the test vessels. PPG recommends instead that DEQ base the aquatic life protection criteria for marine life on the results presented in the enclosed recent technical paper since these results were obtained without the potential synergistic effect of the triethylene glycol carrier solution, and because an actual LC_{50} value is reported, rather than a behavioral aberration end point. The report entitled "Acute Toxicity of Trichloroethylene to Saltwater Organisms" appeared in late 1986 in Bulletin of Environmental Contamination and Toxicology, and is herein presented as Attachment A. Use of this data would result in a marine Acute Toxicity Criteria about 7-10 times higher than that which is presently and incorrectly based on the behavioral end point.

c) Basis for Development of Numerical Criteria for Protection of Aquatic Life is Unknown in Many Cases. For many pollutants, including most volatile organic chemicals and hexachlorobutadiene, the proposed numerical criteria are not based on "Gold Book"

SL 106246

recommended values. It is difficult, if not impossible, to constructively comment on the proposed criteria without knowing the basis of origin of the specific values.

d) Numerical Criteria Should Not be Based on "Advisory" Concentrations. The proposed numerical criteria for both the protection of aquatic life and human health should not be based on EPA advisory levels. It would be more appropriate to wait until testing has been performed and EPA has developed recommended criteria values rather than to proceed at this time and adopt numerical criteria based on EPA advisory levels.

e) Numerical Criteria for Toxics Which Do Not Bioaccumulate Should Not Have Health Criteria Lower than Their MCLs. This is especially true of volatile organic compounds such as benzene, carbon tetrachloride, 1,2-dichloroethane, 1,1-dichloroethylene, trichloroethylene, and tetrachloroethylene (See Attachment B). These all have low water/octanol partition coefficients, and do not represent any significant health threat beyond what one would be exposed to if the water body served as his domestic water supply.

f) Toxic Criteria for Protection of Human Health Should Include Two Sets of Criteria - One Set for Those Stream Segments with "Public Water Supply" and "Propagation of Fish and Wildlife" Designated Uses, and Another for Those without the "Public Water Supply" Designated Use. The "Gold Book" contains two set of recommended human health criteria - one for the case where both contaminated water and contaminated aquatic organisms from the segment are ingested, and another where only contaminated aquatic organisms from the segment are ingested. The former criteria should be used only in those cases where the stream segment has a "public water supply" designated use. These criteria were developed to protect human health in a situation where a person drank two liters of the untreated water each day over a 70-year lifespan. This is clearly different from the situation where an individual swimmer or water skier accidentally and occasionally swallows an insignificant quantity of the water. These criteria are, therefore, inappropriate for segments designated only for "Primary Water Recreation" and not "Public Water Supply".

SL 106247

g) Numerical Criteria for Protection of Health from Carcinogens and Carcinogen Suspects should not all be based on the same 1×10^{-5} risk level. Numerical criteria for protection of health should reflect the actual carcinogenic hazard due to the pollutant, and not regulate all pollutants as equivalent carcinogen hazards. EPA has listed guideline concentrations in the "Gold Book" for three different risk levels (i.e. 1×10^{-5} , 10^{-6} , and 10^{-7}). The World Health Organization's International Agency For Research on Cancer (IARC) is recognized as a leading authority on the evaluation of carcinogenic risk to humans, and periodically publishes a monograph classifying agents it has reviewed from their degree of evidence for carcinogenicity. The latest supplement to that monograph (1987) has classified many of the non-pesticide organic pollutants which Louisiana DEQ has targeted for Toxics criteria as shown in Attachment B. It can be seen that IARC classified only a few of these chemicals as human carcinogens or "probable" human carcinogens (i.e. Group #1 or #2A). Most of them have either been classified as "Possible" human carcinogens (i.e. Group #2B), or "not classifiable as to human carcinogenicity" (i.e. Group #3), or have not been reviewed by IARC because they are not considered to have carcinogenic potency. Where no MCL exists, PPG recommends that Louisiana Water Quality Standards for Toxics should be set as the 1×10^{-5} risk level for IARC Group 1 and 2 A chemicals, and at the 1×10^{-6} risk level for Group 2B chemicals. For Group 3 chemicals and for those remaining toxics for which the "Gold Book" lists health-based criteria, but which IARC has not reviewed, the DEQ's Scientific Advisory Committee (see PPG's Comment A, above) should decide on a case-by-case basis whether a criteria derived by risk assessment is appropriate, and if so, what the appropriate risk level should be.

For comparative purposes, IARC also lists saccharin under 2B Group (i.e. possible human carcinogen), and both cholesterol and actinomycin D under Group 3 (can't be classified).

" Using the variable risk level approach outlined above would result in the selection of "Gold Book" criteria shown underlined in Attachment B.

I. Mixing Zones/Zones of Initial Dilution

1. Guidelines for Delineating Mixing Zones and ZIDs must Accommodate a Wider Range of Condition. The general guidelines for mixing zone on pp 33-35 under Section 1115 "Application of Standards" should be modified to include a broader range of conditions. Presently, they only describe simple, idealized hydraulic systems, rather than complex real-world situations. For example, they don't consider the following conditions:

SL 106248

- Effluent-dominated streams where the discharge volume is large relative to the receiving stream.
- Tidally influenced streams where flow reversal occurs with a periodic frequency.
- Seasonally variable differences in specific gravity between the effluent and the receiving water.

2. Dischargers Should have the Option of Participating in Their Mixing Zone/ZID/Zone of Passage Determination. On pages 33-35 several portions state or imply that the Office of Water Resources of DEQ will unilaterally determine the boundaries of dischargers' mixing zone/ZID/Zone of Passage, and that these will/may become an integral part of future permit conditions. For example, in the first paragraph under D.1 on page 33, the statement is made that:

Mixing zone lengths in flowing water bodies are defined as the distance traveled during one hour at 7Q10 flow. In cases where this is not applicable or when it is determined that this mixing zone does not protect uses, the mixing zone will be established on a case-by-case basis.

On page 34, under Item #6, the statement is made that:

The state shall on a case-by-case basis specify definable, geometric limits for mixing zones.... Applicable limits shall include, but may not be limited to the linear distances from point source discharges, surface area involvement, and volume of receiving water, and shall take into account other nearby mixing zones.

On that same page, under Item #8, it further comments that:

In lakes, estuaries, bays, lagoons, and sounds, the area of mixing . . . will be defined by the Office (i.e., Office of Water Resources within DEQ) on a case-by-case basis.

PPG strongly recommends that this section be reworded to allow dischargers to have the option of participating in the mixing zone/ZID/Zone of Passage Determination process. This should be a cooperative effort rather than one where DEQ unilaterally makes those determinations which will significantly affect the discharger.

3. Definition of "Geometric Limits" for Mixing Zones is Needed. On page 34, under Item #6 of Section 115, there needs to be an explanation of what is meant by the term "geometric limits".

SL 106249

J. In Evaluating the Need for Possible Permit Limits, FDA Action Limits are Appropriate Criteria for Fish and Shellfish as Determined by Tissue Analysis. Section 1121 "Regulation of Point Sources of Toxic Substances Based on the General Criteria" describes under subsection B, the "Implementation and Operation of the Louisiana Water Discharge Permit System." On page 41 under Item 3.c, the following statement appears:

3. When considering water quality outside of the mixing zone, permits will be based on the more stringent criteria developed for protection of human health or protection against chronic toxicity to aquatic life.
 - c. Appropriate permit limits and/or monitoring requirements will be established for dischargers in areas where pollutant concentrations in fish and/or shellfish exceed Food and Drug Administration (FDA) or other emergency action levels as determined by bioconcentration factors or tissue analysis.

FDA Action Levels are the only authorized and appropriate criteria to be used for this purpose, and these should be determined only by tissue analysis; not by application of bioconcentration factors. Recent ecological monitoring studies by USGS in the Calcasieu Estuary have demonstrated that application of bioconcentration factors to predict marine life body burdens is not a reliable technique, and that it may tend to grossly overestimate the concentration of pollutants in biological tissue.

SL 106250

Acute Toxicity of Trichloroethylene to Saltwater Organisms

G. S. Ward,¹ A. J. Tolmsoff,² and S. R. Petrocelli³

¹Environmental Science and Engineering, Inc., P.O. Box ESE, Gainesville, FL 32602, ²PPG Industries, One PPG Place, Pittsburgh, PA 15272, and ³Battelle New England Marine Research Laboratory, Duxbury, MA 02332

Trichloroethylene (TCE) is a chlorinated aliphatic hydrocarbon primarily utilized for vapor-phase degreasing in the fabricated metals industry. Other applications include cold-metal cleaning and use in the manufacture of organic chemicals (Cogswell *et al.* 1982, Chemical Products Synopsis 1984). TCE enters the environment as a result of volatilization during its production and through its industrial uses [U.S. Environmental Protection Agency (EPA) 1980]. TCE has been detected in aquatic environments and organisms at part-per-trillion (ppt) concentrations (Pearson and McConnell 1975). Although TCE is indicated to be widely distributed, relatively limited data exist on the acute effects of TCE on aquatic organisms, especially saltwater species. Results of static acute tests of TCE with a saltwater alga, invertebrate, and fish are reported here to enhance the data base.

MATERIALS AND METHODS

The alga tested was the chain-forming diatom, Skeletonema costatum. The culture was obtained from the EPA Environmental Research Laboratory, Gulf Breeze, Fla., and maintained in stock culture at Bionomics Marine Research Laboratory (BMRL), Pensacola, Fla, according to procedures in U.S. EPA (1978).

Mysid shrimp, Mysidopsis bahia, were born in culture at BMRL and maintained for 3 days before testing. Mysids were reared in natural sea water generally following procedures in U.S. EPA (1978). During holding, temperature was maintained at 22±1°C and salinity at 19 ppt.

Sheepshead minnows, Cyprinodon variegatus, were hatched and reared for 4 to 6 days at BMRL. Sheepshead minnow eggs were spawned naturally in the laboratory in natural sea water basically following procedures in U.S. EPA (1978). During the 48-h period before test initiation, salinity was 19 ppt, and temperature was 22°C. Mortality was <1% during the same period. The fish were 5 to 6 mm total length and averaged 1.4 mg wet weight.

Test water for the algal test was synthetic seawater (Rila Marine Mix) adjusted to a salinity of 30 ppt and enriched with nutrients (U.S. EPA, 1978). Test water for shrimp and fish tests was natural seawater (20 ppt) filtered to 5 μ m.

The alga, S. costatum, was tested in 125-mL flasks containing 50 mL of test solution or control water. Each flask was inoculated with approximately 2.0×10^4 cells/mL. The cultures were incubated at $20 \pm 1^\circ\text{C}$ under 4,300 lux illumination. Test concentrations and controls were triplicated. Measurements of in vivo chlorophyll a were made using a Turner Model III fluorometer after 24, 48, 72, and 96 h of exposure. Cells counts were made after 96 h of exposure using a hemacytometer and Zeiss Standard 14-compound microscope.

Mysids and fish were tested in 1.6-L covered-glass dishes containing 1.0 L of test solution or control seawater. Ten shrimp or fish were tested per dish, and all treatments were duplicated. Shrimp were fed live (48-h old) brine shrimp nauplii on Days 0 and 2 during the test; fish were not fed.

All test organisms were definitively tested in water-soluble fraction (WSF) concentrations of 6.25, 12.5, 25, 50, and 100%. The 100% WSF solution was prepared by adding 1 part TCE to 1,000 parts dilution water (volume to volume) and stirring in a covered Erlenmeyer flask for 1 h. After allowing the solution to settle for 0.5 to 1 h, the WSF was siphoned into another container for distribution to the test containers.

Actual test concentrations of TCE were analytically determined at initiation and termination of the test, or when 100% mortality occurred in a treatment. On Day 0 of the algal test, 300 mL of each test concentration was prepared, and 100 mL was sampled in amber glass bottles with Teflon[®]-coating-lined screw caps. On Day 4 of the algal test, the triplicate test solutions were composited and 100 mL sampled. Composite 100-mL samples were removed from each test solution at initiation and termination of the shrimp and fish tests. The samples were analyzed on the day they were collected.

Based on the results of the tests, 24-, 48-, 72-, and 96-h LC50s or EC50s and 95% confidence limits were calculated, where possible. The computer program generated the LC- or EC50 values using the following statistical methods: moving average angle, probit, and binomial probability (Stephan 1977).

Water samples were transferred into a 250-mL separatory funnel/resin column apparatus prepared as follows. A small plug of glass wool was inserted into a 5-mL pipet and packed lightly into the tip. The pipet was then filled to the top graduation mark with polymeric resin (Mallinckrodt Amberlite[®] XAD-7), leaving about 5 cm of the pipet empty. Using silicone tubing, the pipet top was attached to the tip of a separatory funnel.

The resin column then was rinsed to remove possible contaminants by adding 100 mL of acetone to the separatory funnel and adjusting the stopcock to control the flow of acetone through the resin at approximately 5 mL/minute. Following the acetone cleanup, the column was prepared for use by displacing any acetone remaining on the resin with a 10-mL distilled water rinse. The flow of water through the resin was stopped by closing the separatory funnel stopcock when the water level was approximately 5 mm from the top of the resin.

After addition of the water sample to the apparatus, the stopcock was opened and adjusted to provide a flow-rate through the column of approximately 2 mL/min. The sample was allowed to run completely through the column, leaving the resin dry.

A 10-mL aliquot of nanograde acetone then was added to the separatory funnel and allowed to elute the sample from the resin at about 2 mL/min. A graduated 25-mL concentrator tube was placed under the tip of the resin trap to collect the acetone rinse. The resin trap was allowed to run dry. The 10-mL sample in the concentrator tube contained the trichloroethylene in solution and was diluted as necessary with nanograde n-hexane and analyzed using gas chromatography.

Extracts were analyzed on a Hewlett Packard Model 5880A gas chromatograph equipped with a Nickel-63 electron capture detector and 1.8-m-x-2-mm glass column using the following:

Temperature (°C): Injection port--100
 Oven--25
 Detector--100
Column packing: SP-2250 (1.5%) plus SP-2401 (1.95%) on
 .100/120-mesh Supelcoport
Gas and flow rate: Argon/methane (95%/5%) at 15 mL/min

The mean percentage recovery of three concentrations of TCE added to seawater was 81% with standard deviation of +12%.

RESULTS AND DISCUSSION

The concentration of TCE that dissolved in seawater at 20 ppt or 30 ppt after 1 h of stirring ranged from 232 to 595 ppm. This was within the range of concentrations which could be expected based upon the reported water solubility of 1,000 ppm TCE at 20°C. As expected, based on a vapor pressure of 77 mm Hg, TCE concentrations decreased rapidly from seawater solution through volatilization during the tests. Concentrations of TCE decreased by more than 75% during the first 24 h of exposure, as indicated by four samples, and were less than 3% of initial concentrations after 96 h (Table 1).

Because TCE concentrations rapidly decreased with time and because greater than 90% of all shrimp and fish mortalities occurred during the first 24 h, LC50s were calculated using both average measured concentrations from test initiation and test-

Table 1. Results of chemical analyses of TCE in seawater during 96-h static toxicity tests

Percent water-soluble fraction	Measured concentration (mg/L; ppm)								
	Test Initiation			Test Termination			Average		
	A	B	C	A	B	C	A	B	C
Control	ND	0.06	ND	ND	ND	ND	--	--	--
6.25	17	11	28	ND	0.31	ND	8.5	5.6	14
12.5	24	24	67	ND	0.18	0.01	12	12	34
25	70	51	155	ND	0.01	0.07	35	26	78
50	129	132	237	ND	5.6*	59*	64	69	148
100	300	232	595	ND	28*	119*	150	130	357

A = Results of Skeletonema costatum test.

B = Results of Mysidopsis bahia test.

C = Results of Cyprinodon variegatus test.

ND = Not detected.

*Measurements after 24 hours when 100% mortality observed.

termination samples, and also using initial measured concentrations. The 96-h LC50 values, calculated using initial concentrations, ranged from 27 ppm for mysids to 150 ppm for the diatom (Table 2). The 96-h LC50 values, calculated using averages of initial and final TCE concentrations, were 52 to 63% of the initial concentration values.

Only three other LC50 or EC50 values have been reported for TCE to saltwater organisms prior to this work. Pearson and McConnell (1975) reported LC50 values of 16 ppm and 20 ppm, respectively, for the fish, Limanda limanda, and barnacle nauplii, Elminius modestus, and an EC50 of 8 ppm for the unicellular alga, Phaeodactylum tricornutum. Borthwick (1977), although unable to calculate LC50 values, reported mild intoxication in grass shrimp at 2 ppm and in sheepshead minnows at 20 ppm. These effects subsided after a few hours, but recurred with daily renewals of test solutions. Similar observations were noted in the mysid and sheepshead minnow tests reported here, but at higher concentrations. Sheepshead minnows were observed spinning in the average TCE concentration of 357 ppm, and mysids swam erratically in average test concentrations greater than or equal to 26 ppm. These early effects were followed by death (within 24 h).

Table 2. Calculated 96-h LC50 and EC50 values for saltwater organisms exposed to TCE in static, unaerated seawater*

Organism	EC50 or LC50 (and 95% confidence limits) (mg/L; ppm)	
	Initial measurements	Average measurements
Diatom	150 (139-162)	95 (79-143)
Mysid	27 (19-36)	14 (12-26)
Fish	99 (83-118)	52 (43-64)

*Calculations using initial TCE concentration measurements and average of initial and final measurements.

The LC50 and EC50 values reported here for sheepshead minnow and diatom lie within the range of values reported for TCE in freshwater (i.e., 21.9 to 100 ppm) by Canton and Adema (1978), Alexander et al. (1978), and U.S. EPA (1978), but were much greater than all other values reported for TCE in saltwater (Table 3). Differences in saltwater test results could be attributed to differences in species sensitivity, differences in the type of test system employed, use or non-use of solvent, and/or differences in test temperature. Use of a flow-through system by Pearson and McConnell (1978) in their fish test and stoppered containers for their static tests may be responsible for the greater toxicities observed relative to those measured in the sheepshead minnow and diatom static tests presented herein. However, despite the more vigorous test conditions employed in the invertebrate test by Pearson and McConnell (1978), they reported a higher LC50 value for E. modestus (20 mg/L) than observed herein for the mysid M. bahia (14 mg/L). This certainly confirms that mysids are one of the more sensitive organisms tested to date with TCE.

Differences between TCE test concentrations at which mild intoxication symptoms were observed in test organisms in this study and by Borthwick (1977) may possibly be explained on the basis of carrier solvent synergism and/or temperature effects. Although the grass shrimp P. pugio is generally considered to be a less sensitive organism than the mysid M. bahia, Table 3 shows that Borthwick (1977) reported symptomatic behavior of intoxication in P. pugio at a concentration more than 10 times lower (i.e., 2 mg/L) than observed in this study with M. bahia (>26 mg/L). Variation in toxicity between studies can be lowered by testing with the same species. This is the case with the intoxication symptoms for C. variegatus observed in this study and also those reported by Borthwick (1977). This study reported symptoms at an average TCE concentration of 357 mg/L; the latter

Table 3. Comparison of saltwater toxicity test results reported for TCE (mg/L)

	This Study (Average Concentration)	Other Studies
1. Acute LC ₅₀		
Fish	52 (<u>C. variegatus</u>)	16 (<u>L. limanda</u>) ^a
Invertebrate	14 (<u>M. bahia</u>)	20 (<u>E. modestus</u>)
2. Diatom Algae EC ₅₀	95 (<u>S. costatum</u>)	8 (<u>P. tricornutum</u>)
3. Intoxication Effects (i.e., "spinning," erratic behavior)		
Fish	357 (<u>C. variegatus</u>)	20 (<u>C. variegatus</u>) ^b
Invertebrate	>26 (<u>M. bahia</u>)	2 (<u>P. pugio</u>)

^aPearson & McConnell (1975)

^bBorthwick (1977)

reported them at 20 mg/L. Some of this difference is almost certainly due to the higher temperature (30°C) employed in the Borthwick (1977) study compared to this study (22°C). In addition, the use of a solvent (triethylene glycol) to make the TCE more miscible with the test medium may have potentiated the effects of TCE in some tests.

Enhanced toxicity of TCE and its metabolic products has been reported in man and experimental animals with ethanol (U.S. EPA, 1980). Even the specific solvent utilized may alter the toxicity. Canton and Adema (1978) reported LC₅₀s for D. magna generated among three laboratories of 41 to 100 ppm. No mention was made of the use of solvents. However, when solvents were utilized in tests with D. magna, LC₅₀ values of 85.2 ppm and 18 ppm were determined using acetone and triethylene glycol, respectively (U.S. EPA 1978, Leblanc 1980). These data on D. magna, therefore, suggest a possible increase in TCE toxicity when triethylene glycol is added to enhance its solubility in the test solution.

Since TCE volatilizes from the water so rapidly, it is important to assess the possible consequences of solvents and temperature on the toxicity of TCE. This seems especially true in light of the apparent inversion in relative sensitivity between grass shrimp and mysid tested with TCE. That is, the typically more tolerant grass shrimp tested with solvent and at a higher relative temperature was more sensitive to TCE than the generally acknowledged more sensitive mysid tested at a lower temperature without the aid of a solvent.

Acknowledgments. The authors wish to thank T. Maziarz for his analytical support of these studies and J. Wheat and S. Alexander for their assistance in conducting the tests.

REFERENCES

- Alexander HC, McCarty WM, and Bartlett EA (1978) Toxicity of perchloroethylene, trichloroethylene, 1,1,1-trichloroethane, and methylene chloride to fathead minnows. *Bull Environ Contam Toxicol* 20:344-352
- Borthwick, P.W. (1977) Summarized results of toxicity tests with sheepshead minnows (Cyprinodon variegatus) and grass shrimp (Palaemonetes pugio). U.S. Environmental Protection Agency, Environmental Research Laboratory, Gulf Breeze, Florida
- Canton JH and Adema DMM (1978) Reproducibility of short-term and reproduction toxicity experiments with Daphnia magna and comparison of the sensitivity of Daphnia magna with Daphnia pulex and Daphnia cucullata in short-term experiments. *Hydrobiologia* 59 (2):135-140
- Chemical Products Synopsis (1984) Trichloroethylene. Mansville Chemical Products Corp, Cortland, New York
- Cogswell SA, Bakker J, and Kitai A (1982) CEH Marketing Research Report, C₂ Chlorinated Solvents. Chemical Economics Handbook-SRI International, New York
- LeBlanc GA (1980) Acute toxicity of priority pollutants to water flea (Daphnia magna). *Bull Environ Contam Toxicol* 24:684-691
- Pearson CR and McConnell G (1975) Chlorinated C₁ and C₂ hydrocarbons in the marine environment. *Proc R Soc Lond* 189:305-332
- Stephen CE (1977) Methods for calculating an LC50, ASTM, Aquatic Toxicology and Hazard Evaluation. In: ASTM STP 634. Mayer FL (ed) and Hamelink JL (ed) pp 65-84
- U.S. Environmental Protection Agency (1980) Ambient water quality criteria for trichloroethylenes. EPA 440/5-80-077
- U.S. Environmental Protection Agency (1978) Bioassay procedures for the ocean disposal permit program. EPA 600/9-78-010
- U.S. Environmental Protection Agency. In-depth studies on health and environmental impacts of selected water pollutants. EPA, Contract No 68-01-4646
- Received October 1, 1985; accepted February 4, 1986.

SL 106257

ATTACHMENT B - HUMAN HEALTH CRITERIA
(All concentrations in micrograms per liter except where indicated)

Pollutant	IARC Classif. Group	Primary MCL*	5-88 Draft LA Stds	Suggested "Gold Book" Criteria (micrograms per liter) Related to Carcinogen Risk					
				Consumption of Water & Aquatic Organism			Consumption of Aquatic Organism Only		
				10 ⁻⁵	10 ⁻⁶	10 ⁻⁷	10 ⁻⁵	10 ⁻⁶	10 ⁻⁷
Benzene	#1	<u>5</u>	0.660	6.6	0.66	0.066	400	<u>40.0</u>	4.0
Carbon Tetrachloride	2B	<u>5</u>	0.400	4.0	0.40	0.04	<u>69.4</u>	6.94	0.69
Chloroform	2B		0.190	<u>1.90</u>	0.19	0.019	<u>157</u>	15.7	1.57
Ethylbenzene		(700)	1.400 mg/L	-----1.4 mg/L-----			-----3.28 mg/L-----		
1,2-Dichloroethane (EDC)	2B	5	0.940	<u>9.4</u>	0.94	0.094	<u>2430</u>	243	24.3
1,1,1-Trichloroethane	3	<u>200</u>	200.0	-----18.4 mg/L-----			-----1.83 g/L-----		
1,1,2-Trichloroethane	3		0.600	<u>6.0</u>	0.6	0.06	<u>418</u>	41.8	4.18
1,1,2,2-Tetrachloroethane	3		0.170	<u>1.7</u>	0.17	0.017	<u>107</u>	10.7	1.07
1,1-Dichloroethylene		<u>7</u>	0.033	0.33	0.033	0.003	<u>18.5</u>	1.85	0.185
Trichloroethylene	3	5	2.7	27	2.7	0.27	<u>807</u>	80.7	8.07
Tetrachloroethylene	2B	(5)	0.8	<u>8.0</u>	0.80	0.08	<u>88.5</u>	8.85	0.88
Toluene		(2,000)	14.30 mg/L	-----14.3 mg/L-----			-----424 mg/L-----		
Vinyl Chloride	1	2	2.0	20	<u>2.0</u>	0.2	5246	<u>525</u>	52.5
Bromoform			0.19	<u>1.90</u>	0.19	0.019	<u>157</u>	15.7	1.57
Bromodichloromethane			0.19	<u>1.90</u>	0.19	0.019	<u>157</u>	15.7	1.57
Methylene Chloride	2B		0.19	<u>1.90</u>	0.19	0.019	<u>157</u>	15.7	1.57
Methyl Chloride	3		0.19	<u>1.90</u>	0.19	0.019	<u>157</u>	15.7	1.57
Dibromochloromethane			0.19	<u>1.90</u>	0.19	0.019	<u>157</u>	15.7	1.57
Dichloropropenes	2B		87.0	-----87.0-----			-----14.1 mg/L-----		
Chlorinated Phenols	2B		0.1-0.5	-----Based on organoleptic consid.-----					
Phenol (Total)			5.0	-----3.5 mg/L-----					
Benzidine	1		0.120ng/L	1.2ng/L	0.12	0.01	5.3	0.53	0.05
Hexachlorobenzene	2B		0.720ng/L***	7.2ng/L	0.72	0.072	7.4ng/L	0.74	0.074
Hexachlorobutadiene	3		0.450	<u>4.47</u>	0.45	0.045	<u>500</u>	50	5.0
Arsenic	1**	(30)	50	22 ng/L	2.2	0.22	175	17.5	1.75
Chromium III	3	(100)	50	-----170 mg/L-----			-----3,433 mg/L-----		
Chromium VI	1**	(100)	50						
Zinc			5.0 mg/L						
PCBs	2A	(0.5)	.079 ng/L***	0.79 ng/L	0.079	0.0079	0.79	0.079	0.0079

IARC Group 1 = Carcinogenic to humans
 2A = Probably carcinogenic to humans
 2B = Possibly carcinogenic to humans
 3 = Not classifiable as to its carcinogenicity to humans

* Bracketed values have been proposed.

** This evaluation applies to the group as a whole and not necessarily to all individual chemicals within the group.

*** MDL for PCB = 50 ng/L; MDL for PCBs = 65 ng/L