AD-A034 461 NATIONAL ACADEMY OF SCIENCES WASHINGTON D C COMMITT--ETC F/G 15/5
SYSTEM FOR CLASSIFICATION OF THE HAZARDS OF BULK WATER TRANSPOR--ETC(U)
SEP 75 DOT-CG-41680-A
UNCLASSIFIED USCG-D-126-76 NL

1 OF 1
ADA034461

END
DATE
FILMED
2 - 77

REPORT NO. CG-D-126-76

SYSTEM FOR CLASSIFICATION OF THE HAZARDS OF BULK WATER TRANSPORTATION OF INDUSTRIAL CHEMICALS

SEPTEMBER 1975

FINAL REPORT

Document is available to the U.S. Public through the National Technical Information Service, Springfield, Virginia 22161

PREPARED FOR

U.S. DEPARTMENT OF TRANSPORTATION

UNITED STATES COAST GUARD

OFFICE OF RESEARCH AND DEVELOPMENT

WASHINGTON, D.C. 20590

NOTICE

This document is disseminated under the sponsorship of the U. S. Department of Transportation in the interest of information exchange. The United States Government assumes no liability for the contents or use thereof.

The United States Government does not endorse products or manufacturers. Trade or manufacturers' names appear herein solely because they are considered essential to the object of this report.

18 19

Technical Report Documentation Page

1. Report No. US CG-D-126-76	2. Government Accession No.	3. Recipient's Catalog No. 11
4. Title and Subtitle 6 System for Classification of the Hazards of Bulk Water Transportation of Industrial Chemicals.		5. Report Date Sep~~tember~~ 1975
		6. Performing Organization Code
7. Author(s) Committee on Hazardous Materials 12 49p.		8. Performing Organization Report No.
9. Performing Organization Name and Address National Academy of Sciences, Washington, D. C. 20418		10. Work Unit No. (TRAIS) 3121.11
		11. Contract or Grant No. 15 DOT-CG-41680-A
12. Sponsoring Agency Name and Address U. S. Coast Guard, Office of Research and Development, Marine Safety Technology Division, Washington, D. C. 20590		13. Type of Report and Period Covered 9 Final Report.
		14. Sponsoring Agency Code G-DSA-1

15. Supplementary Notes

The U. S. Coast Guard Office of Research and Development's Technical Representative for the work performed herein was Dr. John M. CeCe

16. Abstract

NR

The first version of this report was prepared in 1966 by the Committee on Hazardous Materials, a committee in the Division of Chemistry and Chemical Technology of the National Research Council, in response to a request from the Coast Guard for a systematic guide to rating the relative hazards of chemicals and other materials shipped in bulk over the waterways. This 1975 report reflects major changes which we feel improve the system. ~~We believe~~ that the study, though of restricted scope, may be of interest to other groups concerned with assessing hazardous aspects of chemicals, and ~~we also believe~~ that future studies of this nature will benefit from criticism of the present effort. We are publishing the report for wider circulation in its present form, calling the attention of the reader to the limitations noted in the introductory section. The Committee will welcome any general suggestions or specific criticism that will improve the usefulness of such a hazard-rating guide.

should

It is felt

17. Key Words	18. Distribution Statement
Hazardous Materials Classification System Water Transportation	Document is available to the public through the National Technical Information Service, Springfield, Virginia 22161

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of Pages	22. Price
Unclassified	Unclassified	47	4B

Form DOT F 1700.7 (8-72) Reproduction of completed page authorized

407 196

NATIONAL RESEARCH COUNCIL
Assembly of Mathematical and Physical Sciences
Office of Chemistry and Chemical Technology

COMMITTEE ON HAZARDOUS MATERIALS

FOREWORD

The first version of this report was prepared in 1966 by the Committee on Hazardous Materials, a committee in the Division of Chemistry and Chemical Technology of the National Research Council, in response to a request from the Coast Guard for a systematic guide to rating the relative hazards of chemicals and other materials shipped in bulk over the waterways. This 1975 report reflects major changes which we feel improve the system. We believe that the study, though of restricted scope, may be of interest to other groups concerned with assessing hazardous aspects of chemicals, and we also believe that future studies of this nature will benefit from criticism of the present effort. We are publishing the report for wider circulation in its present form, calling the attention of the reader to the limitations noted in the introductory section. The Committee will welcome any general suggestions or specific criticism that will improve the usefulness of such a hazard-rating guide.

R. B. Beckmann, Chairman
Committee on Hazardous Materials

PREFACE

The U.S. Coast Guard has requested the assistance of the Committee on Hazardous Materials of the National Research Council in developing a system of classifying the potential hazard associated with the water transportation of industrial chemicals in bulk.

Numerous schemes for assessing the hazards of materials have been developed by various organizations, but none completely fulfills the Coast Guard requirements, since most of the existing schemes have been developed for purposes other than assessment of hazard in bulk water transportation. It was also suggested by the Coast Guard that the system of hazard classification should deal with the several kinds of hazards presented in varying degrees by individual chemicals.

This is a report of results, to date, of the efforts of the Committee on Hazardous Materials to develop and evolve a scheme of hazard classification. The hazard classification system described in this report employs four main classes of hazards: fire, health, water pollution, and reactivity; and further subdivides the health, water pollution, and reactivity into subclasses. Under each class or subclass, a numerical rating is given to indicate the relative degree of potential hazard. General guidelines were developed to describe five levels of severity for each. It should be borne in mind that these ratings relate to hazardous situations that may arise in the marine transportation of the materials under consideration, and are not necessarily applicable to other situations.

TABLE OF CONTENTS

INTRODUCTION

The purpose of this system is to provide the parametric and procedural guidelines for making a comprehensive and consistent profile that reflects the inherent hazards of chemical and other cargoes transported in bulk by water. As used here, inherent refers to the hazards presented to life and property from the cargo itself when accidentally released, without consideration of the method or quality of its containment. Under normal ambient conditions the cargo may be a gas, a liquid, or a solid, but this system places greater emphasis on hazards of shipments in the liquid phase. Solids are considered only if shipped molten or in solution. Classification requires identification of the hazards and the comparative rating of each according to established guidelines. The intended use of the resulting hazard profile is to help the Coast Guard toward a more complete understanding of the requirements necessary to insure safe moving, handling, loading, and unloading procedures which collectively constitute the bulk water transportation system.

The classification system from which the present one has evolved was developed by the Committee during 1965-66 by a panel headed by Mr. Robert F. Barker. It is described in National Academy of Sciences publication No. 1465, EVALUATION OF THE HAZARD

OF BULK WATER TRANSPORTATION OF INDUSTRIAL CHEMICALS - A Tentative Guide, published in 1966, and is based on a simple numerical scale of 0, 1, 2, 3, 4 indicating an increasing degree of hazard in each of nine independently described types of hazards. It was revised in 1971 under the Chairmanship of Dr. W. W. Crouch and in 1974 under the Chairmanship of Mr. William H. Doyle.

It is still beyond the state of our present knowledge to devise hard and unequivocal definitions that would permit rating the wide variety of chemical cargoes in a completely objective and unambiguous manner. Many variables exist which cannot be taken into account in such definitions. For example, certain materials have no flash point or fire point by accepted techniques of determination and yet, under certain conditions of elevated temperature and high energy ignition source, either will ignite or decompose. To rate these materials as "nonflammable," in the context of past use of that classification, would ignore the hazard which we know exists.

Following publication of the 1966 and subsequent editions of the system, comment was received from several sources, including IMCO*, the Netherlands, and the United Kingdom, which suggested the need for further extension and amplification of the guidelines so as to define the ratings more precisely. The Committee has given careful consideration to all comments and has

*Intergovernmental Maritime Consultative Organization, a U.N. agency.

evolved the present system which, we believe, is an improvement because it makes the rating criteria more precise and less subjective. The section on Health Hazards results from suggestions from the NRC Committee on Toxicology and Mr. Ralph C. Wands, Director of the NRC Advisory Center on Toxicology. The section on Reactivity Hazards was developed by Professor William A. Cunningham in close cooperation with Professor Roy W. Hann, Jr., Dr. James P. Flynn of The Dow Chemical Company, Mr. William H. Doyle of Factory Insurance Association (Retired), and others.

In developing the system, the Committee has not been concerned with the regulations resulting from application of this information by the Coast Guard or by others. The fixing of a hazard profile by use of the criteria is not intended to suggest that the Committee recommends any specific regulation of the chemical or any unusual protective measure. The Committee is evaluating <u>inherent</u> hazards. As in all hazard classifications, the system in which the material is encountered is as important as the material itself, if one is to be objective in the determination of relative risk. For this reason, <u>responsible judgment is essential in applying the profiles</u>. The secondary and incidental effects of an accidental release, such as incapacitation of individuals at critical controls, which in turn could affect adversely other operations, exemplifies the need for consideration of the complete system, not the hazards of the material alone.

While it is our belief that this revised system represents an improvement, absolutes are seldom obtained in an imprecise and changing world, and any comments either regarding the general classification system or regarding specific criteria will be welcomed by the Committee.

The Committee cautions the reader that each number in the classification system is intended to reflect a ranking with respect to a particular phase of the total hazard, and each number should be carefully considered by itself. Any attempt to use mathematical operations to produce an index or composite in the form of one number should be discouraged, since such oversimplification can produce confusion and misunderstanding.

The classification consists of consideration of nine parameters, which are reflected by nine columns. These are described in the following section of guidelines. The nine columns are:

Column I	Fire Hazard Rating
Column II	Hazard Rating for Contact of Liquid with Skin and Eyes
Column III	Hazard Rating for Inhalation of Vapors (Occasional Short Term)
Column IV	Hazard Rating for Inhalation of Gases (Occasional Short Term)
Column V	Hazard Rating for Repeated Inhalation of Gases and Vapors
Column VI	Water Pollution Hazard Rating - Human Toxicity
Column VII	Water Pollution Hazard Rating - Aquatic Toxicity
Column VIII	Water Reaction Hazard Rating
Column IX	Self-Reaction Hazard Rating

Reactivity with other chemical cargoes, considered in the earlier editions of the evaluation system, is now treated in a separate document (see page 29).

Previous editions of this system included a section on aesthetic effects of water pollution, as distinguished from hazardous effects. While fully recognizing the importance of aesthetic values to water quality, the Committee was not able with present knowledge to devise a rating system to evaluate chemicals with the same objectivity used for the other hazards. Therefore, pending further information, the Committee deferred consideration of the problem and has deleted the aesthetic evaluation from this edition.

GUIDELINES

COLUMN I - FIRE HAZARD RATING

Chemicals are classified as having a fire hazard (a rating above zero) if their properties are such that during bulk water transportation they may ignite, spread fire, or produce an ignitable mixture of vapor and air in the ullage* of the container. Heat released by burning liquids is always a personnel hazard; therefore, ratings are based principally on flash points which are a guide to probability of fire. Where appropriate, notations are included to relate the evaluation to unusual or unsuspected hazards which may arise from unique or inadequately understood characteristics. For example, (a) chemicals containing halogens, nitrogen, and sulfur evolve noxious or corrosive gases during combustion or decomposition; (b) certain chemicals have exceptionally high or low ignition temperatures; and (c) certain chemicals ignite spontaneously on contact with air or water. The specific grades are described more fully below.

Table I - FIRE HAZARD

Grade 0	Insignificant Hazard: Includes chemicals that are essentially noncombustible.
Grade 1	Slightly Hazardous: Includes chemicals having a closed-cup flash point above 140°F (60°C).
Grade 2	Hazardous: Includes combustible chemicals having a closed-cup flash point below 140°F (60°C) and above 100°F (37.8°C).

* Ullage - that space of the whole cargo container not occupied by the cargo itself.

Table I - FIRE HAZARD, continued

Grade 3	Highly Hazardous: Includes flammable liquids having a closed-cup flash point below 100°F (37.8°C) and a boiling point under standard conditions above 100°F (37.8°C).
Grade 4	Extremely Hazardous: Includes volatile liquids or liquefied gaseous materials having a flash point below 100°F (37.8°C) and a boiling point below 100°F (37.8°C).

Open-cup flash points are used when closed-cup data are not available. For this application, an open-cup flash point of 115°F (46.1°C) is employed in place of a closed-cup figure of 100°F (37.8°C), and an open-cup temperature of 160°F (71.1°C) is used in place of 140°F (60.0°C) closed-cup. Unless the limits of accuracy of the flash point determinations are known, the number may be questioned, since much uncertainty accompanies many "literature" values, and many values do not specify by what method they were determined, or the purity of the substance tested.

The purity of the material in transport may differ significantly from the material on which the determination was made, so significant differences may be encountered.

Unless specified to the contrary, flash points should be determined according to methods prescribed in NFPA 321, Basic Classification of Flammable and Combustible Liquids, available from the National Fire Protection Association, 470 Atlantic Avenue, Boston, Mass. 02210.

Problems of electrical ignition characteristics, as reflected by Article 500 of the National Electrical Code, and considerations of intrinsic safety of electrical equipment in explosive or combustible atmospheres, are beyond the scope of this evaluation system.

HEALTH HAZARD RATINGS

This portion of the profiles applies to the occupational health hazards to personnel immediately associated with the water-borne transportation of materials in bulk on ship, dock, or at a marine terminal. Liquids and gases are considered separately because of their different modes and areas of contact with the body. Since fluids escaping from pressurized storage or piping systems may take the form of a mist or aerosol, this distinction is somewhat blurred. Gases are considered herein to be those substances having a vapor pressure of at least 40 psi at 70°F (21°C) or 104 psia at 130°F (54°C). Their major health hazard results from inhalation, although gas spilled as refrigerated liquid can cause freezing of tissue analogous to burns. The major hazard with liquids is from direct contact. It may involve toxicity, corrosion, or burns if the liquid is hot. Also, vapors from spilled liquids may be inhaled. In these profiles the likelihood of injury from such inhalation is related to the vapor pressure of the liquid at 122°F (50°C).

The profiles are intended for the guidance of the Coast Guard with respect to people involved in the water transportation system.

They are not based on hazards to the general public arising from transportation accidents. Such considerations are more properly the concern of agencies such as the Food and Drug Administration and the Environmental Protection Agency.

Recognizing the advantages in uniformity of toxicity testing procedures, the methods of the Department of Transportation, Office of Hazardous Materials, have been adopted. These have been derived from and correlated with similar regulations of the Food and Drug Administration and the Pesticide Programs Office of the Environmental Protection Agency.

Such uniform toxicity data on a material can be used in combination with information on its chemical and physical characteristics to rank its health hazard in the areas of interest. For these profiles the areas are contact of liquid with skin or eyes, and inhalation on the basis of occasional short term as in a single incident, as well as repetitive as in daily work exposure. The rankings range from 0, for materials which are not expected to produce injury or temporary incapacitation, but which may cause transient and fully reversible effects, to 4 for those where there is probability of death as a result of a transportation accident leading either to an inhalation exposure or to contact with the skin.

There are a few chemicals that may be transported which might present an unusual hazard during accidents. It is recommended that the NRC Committee on Toxicology supplement its hazard ratings by calling to the Coast Guard's attention those materials which, in their judgment, have a reasonable possibility of producing carcinogenic or mutagenic effects in humans from single short exposure.

COLUMN II - HAZARD RATING FOR SKIN AND EYE CONTACT

Liquids have been evaluated with reference to the potential for harm from splashes and other accidental contact with the skin and eyes. Skin and eyes are highly vulnerable to damage by many chemicals -- a consideration frequently overlooked in day-by-day operations.

The rating scheme for such contact is given in Table II.

Table II - LIQUID CONTACT WITH SKIN AND EYES HAZARD

Grade 0	Insignificant Hazard: Liquids in this category are all those not described below.
Grade 1	Slightly Hazardous: Liquids that are corrosive to the eyes according to the definition in 16 CFR 1500.3(c)(3) and the test procedure in 16 CFR 1500.42
Grade 2	Moderately Hazardous: Liquids in this category are: A. Liquids that are corrosive according to the test procedure described in 46 CFR 146.23-1. B. Materials that are transported as liquids at 140°F (60°C) or above. C. Liquefied gases that are capable of causing freeze burns.

Table II continued

Grade 3	Highly Hazardous: Liquids in this category have an LD_{50}* of more than 20 milligrams per kilogram of body weight when administered by continuous contact for 24 hours or less with the bare skin of rabbits, according to the test procedure described in 21 CFR Section 191.10 of the Code of Federal Regulations.
Grade 4	Extremely Hazardous: Liquids in this category have an LD_{50}* of 20 milligrams per kilogram or less of body weight when administered by continuous contact for 24 hours or less with the bare skin of rabbits, according to the test procedure described in 21 CFR Section 191.10 of the Code of Federal Regulations.

COLUMN III -- HAZARD RATING FOR INHALATION OF VAPORS (Short Term)

Substances have been evaluated with reference to the potential of injury from single short-term exposures by inhalation of vapors. Although the vapor pressure measurements data regarding volatile materials are often available in the literature, care must be exercised in relating vapor pressure to the characterization of hazards from specific spill situations. Other parameters are involved in the evaporation and generation of a vapor cloud and may be more significant in specific situations than vapor pressure.

The rating scheme for such inhalation exposure is given in Table III.

---

* LD_{50}, That dose likely to kill one-half of a group of animals within 14 days

LC_{50} That concentration which, over a given period of time, is likely to kill one-half the test animal species.

Table III - INHALATION OF VAPORS (Occasional Short-Term)

Grade 0 Insignificant Hazard: Liquids in this category are all those not described below.

Grade 1 Slightly Hazardous: Liquids in this category cause dizziness and unsteadiness in 30 minutes or less upon exposure to an atmosphere saturated with vapor at 122°F (50°C). See footnote.*

Grade 2 Moderately Hazardous: Liquids in this category have an LC_{50} ** in air of more than 200 parts per million (ppm) but not more than 2000 ppm by volume of vapor; or more than 2 milligrams per liter, but not more than 20 milligrams per liter of mist when administered by continuous inhalation for one hour or less to both male and female albino rats (young adults), provided the Coast Guard finds that such concentration is likely to be encountered by man under any reasonably foreseeable conditions of transportation. See footnote.*

Liquids in this category may produce sufficient irritation of the eyes or respiratory tract to cause temporary incapacitation. This includes lachrymators and those corrosive liquids as defined above in Table I that have a vapor pressure at 122°F (50°C) of 10 mm Hg or more. See footnote *

Grade 3 Highly Hazardous: Liquids in this category have an LC_{50}** in air of more than 50 ppm but not more than 200 ppm by volume of vapor, or more than 0.50 milligrams per liter, but not more than 2 milligrams per liter of mist when administered by continuous inhalation for one hour or less to both male and female albino rats (young adults), provided the Coast Guard finds that such concentration is likely to be encountered by man under any reasonably foreseeable conditions of transportation. See footnote. *

---

* During transportation emergencies involving liquids (ruptures, spills, etc.) the degree of personnel hazard is increased by rapid evaporation. If the ratio of the evaporation rate for the test material to that of n-butyl acetate at 122°F (50°C) under the same test conditions is 0.8 or less, the test material should be given the next higher rating with a notation to this effect. An appropriate test procedure has been described.

NOTE: Footnotes * and ** are continued at bottom of next page.

Table III continued

Grade 4 Extremely Hazardous: Liquids in this category have an LC_{50}** in air of 50 parts per million by volume or less of vapor, or 0.5 milligrams per liter or less of mist when administered by continuous inhalation for one hour or less to both male and female albino rats (young adults), provided the Coast Guard finds that such concentration is likely to be encountered by man under any reasonably foreseeable conditions of transportation.

COLUMN IV - HAZARD RATING FOR INHALATION OF GASES (Short Term)

Substances have been rated with regard to potential for injury from occasional short-term inhalation of gases.

The rating scheme for such inhalation is given in Table IV:

Table IV

Grade 0 Grade 0 is not applicable since no gas has an insignificant hazard.

Grade 1 Slightly Hazardous: Gases in this category are all those not described below since the release of a gas into a confined space may displace sufficient oxygen to create a significant hazard to life.

Grade 2 Moderately Hazardous: Gases in this category have an LC_{50}** in air of more than 200 parts per million but not more than 2000 parts per million by volume of gas when administered by continuous inhalation for one hour or less to both male and female albino rats (young adults).

---

*Continued from page 12

1) Wilson, L. D., "Evaporation Rates of Solvents and an Improved Method for their Determination," Paint, Oil and Chemical Review, Vol. 118, No. 24, p. 6, Dec. 1 (1955).
2) Wilson, L. D., "Evaporation Rates of Solvents - An Extension of Earlier Studies," Paint Industry Magazine, Vol. 76, No. 4, p. 15, April (1961).

**See footnote Table II, page 11.

Grade 2 of Table IV continued

Gases in this category may produce sufficient irritation of the eyes or respiratory tract to cause temporary incapacitation. This includes lachrymators.

Grade 3 Highly Hazardous: Gases in this category have an LC_{50}** of more than 50 ppm but not more than 200 ppm as described in Grade 3 of Table III.

Grade 4 Extremely Hazardous: Gases in this category have an LC_{50}** of 50 ppm or less as described in Grade 4, Table III.

COLUMN V - HAZARD RATING FOR REPEATED INHALATION OF GASES AND VAPORS

Since the repeated exposure of inhalation of gases and vapors may produce effects different from occasional short-term inhalation, substances have been evaluated for repeated inhalation exposures.

The intent of these tables of Hazard Rating is to provide a relative ranking of occupation health hazards for transportation workers. The circumstances of these repeated exposures to materials in transport are sufficiently similar to the concepts utilized in setting standards for other industrial workers to warrant utilizing the OSHA (Occupational Safety and Health Act, P.L. 91-596, 29CFR Section 1910.93) standards for developing the relative rankings.

The rating scheme for repeated inhalation is given in Table V:

** See footnote Table II, page 11

Table V* - HAZARD RATING FOR REPEATED INHALATION OF GASES AND VAPORS

Grade 0	Insignificant Hazard: Materials in this category are all those not described below and having standards established by the U.S. Department of Labor, Occupational Safety and Health Administration (OSHA), as in 29 CFR Subpart G, Section 1910.93, of 1000 ppm or more.
Grade 1	Slightly Hazardous: Materials in this category have standards established by OSHA of 100 ppm or more but less than 1000 ppm.
Grade 2	Moderately Hazardous: Materials in this category have standards established by OSHA of 10 ppm or more but less than 100 ppm.
Grade 3	Highly Hazardous: Materials in this category have standards established by OSHA of 1 ppm or more but less than 10 ppm.
Grade 4	Extremely Hazardous: Materials in this category have Occupational Safety and Health Standards established by OSHA of less than 1 ppm.

* These OSHA standards are applicable to a normal working situation, i.e., 8 hours per day, 5 days per week.

WATER POLLUTION HAZARD RATING

The water pollution characteristics of chemicals are rated in Columns VI and VII of Table XI. These ratings are intended to reflect the degree of concern that arises when a specified chemical is for any reason spilled or dumped into waterways. A wide variety of problems may arise from such occurrences: water for municipal systems may be made unfit for human consumption; fish and other aquatic life may be killed; waters in streams or on beaches may be contaminated by oily, sticky, dark-colored, or malodorous materials which make them unfit for recreational purposes; or noxious odors or vapors may evolve from polluted water to contaminate the atmosphere in areas nearby.

The water pollution characteristics of chemicals are rated in two ways: (1) human toxicity, and (2) aquatic toxicity. In the case of both the human toxicity and aquatic toxicity ratings, it is imperative that the user recognize that these are total dose and concentration toxicity values. The use of these numbers in developing design requirements or governmental regulations must be predicated on the quantity of material which could potentially be discharged to the aquatic environment and on the physical, chemical, and biologic properties of the aquatic system. For example, a small discharge of a material toxic in relatively low concentration into a small (or static) aquatic system could result in catastrophic consequences to the particular system.

A detailed discussion of the interrelationship of discharge size, system properties and toxicity values is presented following the description of the aquatic toxicity rating system.

COLUMN VI - HUMAN TOXICITY

It is recognized that ingestion of water contaminated by polluting substances may produce both acute and long-term reactions. In dealing with this problem, the Committee chose to consider it as one of acute toxicity in that consumption of contaminated water resulting from transportation of chemicals is likely to be rare and to extend over a short time period. The degrees of hazard are listed in terms of *the median lethal dose* (LD_{50}) *of the substance.* While it is desirable to base the LD_{50} figures on knowledge of the weights of substances likely to be ingested in water, the precise data from which these can be calculated are not available. The Committee therefore rated this hazard in terms of the oral LD_{50} values, as determined in suitable mammalian species, on the assumption that the hazard increases with toxicity.

The Committee recognizes that this assumption may be modified in the individual case by factors such as degradation of the contaminating substances by water or aquatic life and the extent, if any, of their removal by water treatment processes or evaporation. It was also recognized that LD_{50} values may be different when determined on pure chemicals and on the dilute solutions such as occur in polluted water. Despite these facts, and because the factors discussed would reduce rather than increase the hazard from particular chemicals, the Committee felt that rating in terms of the mammalian oral LD_{50} figures was valid as an indication of the potential toxic hazard from ingestion of contaminated water.

Ratings are reduced below those developed by the above procedure, for compounds that have low water solubility (and accordingly cannot reach a high concentration in water), for compounds of high volatility (that vaporize in a short time from the surface), and for compounds that have a pronounced taste or odor which will serve as a warning to prevent human consumption.

The hazard has been rated in five groups ranging from "Insignificant Hazard" (LD_{50} 5000 mg/kg**) to "Extremely Hazardous" (LD_{50} 5 mg/kg body weight) as shown below.

Table VI - WATER POLLUTION HAZARD RATING
HUMAN TOXICITY

Grade	Description	LD_{50}
0	Insignificant Hazard	Above 5000 mg/
1	Slightly Hazardous	500-5000 mg/kg
2	Moderately Hazardous	50-500 mg/kg
3	Highly Hazardous	5-50 mg/kg
4	Extremely Hazardous	Below 5 mg/kg

** See Footnote Table II, page 11

The Committee emphasized that description of a substance as non- or slightly hazardous does not indicate that water polluted with this substance is safe for drinking. A completely different set of toxicological criteria is needed to define the standards for potable water for municipal supplies.

Detailed information on data sources and decision rationale is maintained in the offices of the Committee in Washington, D. C.

COLUMN VII - AQUATIC TOXICITY

Chemicals are rated in Column VII on the basis of their toxicity to aquatic life. Fish were selected as one of the most sensitive groups for which toxicological data are available with information on shrimp and other aquatic organisms being used to fill in the gaps. The 96 hour TL_m * was used to provide the basis for making five rankings of the toxic potential. It was considered that if the substance would not be lethal according to this test at greater than 1000 ppm (mg/l) then it posed no toxic hazard to aquatic life. Intertidal areas subject to the spillage should be given careful consideration because toxic effects can be enhanced with exposure - i.e. insoluble oils.

Consistent with the rating of other pollution hazards, these ratings should be reduced in some cases for chemicals having such low

---

*TL_m - The concentration of a substance which, within the specified time (generally 96 hours), will kill 50% of the exposed group of test organisms, often specified in parts per million (mg/l). The TL_m test may be conducted under static or continuous flow conditions.

water solubility and high volatility, that they will not normally contaminate waters. However, those chemicals with low solubility and/or low density that can interfere with gas interchange across the air-water interface, or with a marked tendency to emulsify can be a significant pollutant. Detailed data and information on their sources and decision rationale are maintained in the offices of the Committee in Washington, D.C.

For many of the chemicals no published aquatic toxicity data are available. In these cases, the ratings in Table XI were estimated from physical properties and by analogy with data from chemically similar compounds. When information was available for more than one aquatic organism, the figure for the most susceptible species was generally used.

The system rankings are outlined below.

Table VII - HAZARD RATING - AQUATIC TOXICITY

Grade	Description	TL_m Concentration
0	Insignificant Hazard	>1000 mg/l
1	Practically nontoxic	100-1000 mg/l
2	Slightly toxic	10-100 mg/l
3	Moderately toxic	1-10 mg/l
4	Highly toxic	<1 mg/l

Most of the 96 hr TL_m test data available were derived from tests with adult or juvenile aquatic organisms usually from upper levels of the food chain. The Committee recognized however, that other stages, e.g. larvae or eggs, or organisms lower but critically important in the food web, might be much more susceptible than the organisms or stage of organism tested.

Although the Committee recognized that at the present time acute toxicity TL_m data are more complete and therefore present the best method of ranking substances according to hazard, it was aware that chronic or sub-lethal effects may ultimately be more important ecological considerations. Fish can detect concentrations as low as 10^{-3} to 10^{-8} mg/l of a range of substances. Behavior and chemo-reception (as involved in food finding, mating, migration) might be adversely affected by concentrations considerably lower than indicated by the 96 hr TL_m test. Physical properties of materials are often of great significance and should be considered.

SPECIAL NOTATIONS IN COLUMN VII

Several special notations are used to call attention to particular chemical properties of significance with regard to living aquatic resources. These are described below.

A. Bioaccumulation

Bioaccumulation occurs if an aquatic organism takes up a chemical to which it is exposed so that it contains a higher concentration of that substance than is present in the ambient water or its food. The process is reversible. Where the rate of metabolism or elimination of the substance is high and the degree or period of exposure small, bioaccumulation may be short-lived. Where the rates of metabolism and elimination are low or the degree or period of exposure great, bioaccumulation may be of long duration. The Committee also recognized that metabolites may be formed from ingested substances which may be more poisonous or ecologically damaging and/or have a longer biological half life than the original polluting material, e.g., DDT $\longrightarrow$ DDE.

The hazard presented by a substance is increased if it is accumulated in aquatic organisms since these may eventually be poisoned. (In addition, certain substances concentrate in the parts of fish and shellfish which, if eaten by man, result in accumulation in human tissues. This accumulation may be a hazard to human health.)

The following are examples of potentially harmful substances whose release into water must be avoided because they degrade slowly, if at all, and therefore tend to accumulate in the aquatic ecosystem:

Aldrin
BHC isomers
Cadmium compounds
Chlordane
DDT
Dieldrin
Endrin
HCB (Hexachlorobenzene)
Heptachlor (Epoxides)
Lead compounds
Mercury compounds
Polyhalogenated biphenyls

B. Biochemical Oxygen Demand

Many materials which are nontoxic or below toxic level in the classical sense may destroy aquatic life if the degredation of the material removes the dissolved oxygen from the aquatic system. For example, in a relatively static system such as a lake or a gulf coast estuary, a material with a 1/1 oxygen demand (i.e., 1 lb. of oxygen demand for 1 lb. of material) would deplete the total oxygen resource under summer conditions at concentrations as low as 5-10 mg/l. This potential harm to the aquatic community has not been rated at this time because the volume, flow, initial dissolved oxygen concentration, and reaeration rates vary with different aquatic systems and because oxidation rates (i.e., decay rates) for materials vary and are not readily available. Where the potential of high oxygen demand exists for relatively nontoxic materials, the notation "BOD" is used to warn that a potential hazard of oxygen depletion may exist.

C. Insoluble Materials

Insoluble materials whose discharge may blanket the living resources on the bottom of aquatic systems or prevent gas exchange at the surface may be significant. A notation of "D", when used, indicates that this may be a potential problem.

<u>Evaluation of Potential Discharges</u>

The illustrative computations in Appendix 1 were developed to demonstrate the relationship between a quantity of a discharged material, the properties of aquatic systems which may be receiving the material and the resulting concentration of the material. It must be pointed out that the prediction of water quality profiles in aquatic systems is complex and is still being developed.

The importance of currents, turbulent mixing and diffusion to dilution and dispersion of materials introduced into the aquatic environment is fully recognized and reasonably well understood. Modifying factors such as stratification, caused by fresh-water run-off, solar heating, and heat of solution or dilution are qualitatively understood, but have been evaluated in only a few instances.

Perhaps of secondary importance, but often significant are the effects of the physical and chemical characteristics. Waters heavily loaded with suspended materials from either natural or man-made sources will interact with introduced substances in a different way from clear waters. For example, colloidal suspensions of clay in fresh water will adsorb certain chemicals including nutrients which will be precipitated as the clay is flocculated on mixing of fresh water with sea water. These materials may be fixed in the sediments or could leach into the overlying water to affect bottom fishes and other organisms.

There could be chemical interaction of dissolved organic and inorganic materials in the receiving waters with introduced substances. A neutralization or antagonism of one substance toward another sometimes occurs to alter the ultimate effect on aquatic organisms. Examples are some heavy metals which are less harmful in sea water and hard fresh water than in soft fresh water. On the other hand, there may be synergism where materials interact to produce a harmful effect on organisms, that is far more than additive. In some instances, such as with endosulfan, the toxicity is higher in saline water than in fresh water.

This short document cannot describe fully the large number of inherent combinations of the character of the discharged material and the receiving system's physical and chemical properties. However, some generalized assumptions can be made which will permit those concerned with regulation of shipping or other potential discharge to have some feeling for the relationship between system and discharge characteristics and the numerical values used to evaluate the aquatic toxicity hazard of various materials. As a result those concerned with regulation will have some rough idea of the magnitude of concentrations and the problem with which they might have to cope in different types of aquatic systems.

In each of the examples in Appendix 1 assumptions which were made have been carefully specified along with those systems and material characteristics or properties which need to be considered in a more detailed analysis. The hypothetical systems were chosen on the basis of an evaluation of real aquatic systems of which the Committee had intimate knowledge. These are major navigable systems currently in use by commercial shipping in the United States.

Substantial information as to the specific size of discharges of material in different ranges of toxicity may be derived from the examples provided in Appendix 1. Extreme caution is recommended, however, to ensure that the results are not extrapolated to systems substantially different from those described or used in such a way as to ignore background environmental stresses or concurrent effects from other materials discharged into the system. They do NOT indicate safe discharge levels but are intended only as an indication of what might be harmful in the rather special hypothetical areas described.

By extrapolating Table A in Appendix 1, it may be determined that from 3 to 30 tons of a material with a 3 rating in Column VII of the Rating Table (TL_m= 1 - 10 mg/l), (depending on toxicity within the range), would cause death of a coastal area community with a 1/4 mile square area 60 ft. deep. From 50 to 500 tons would cause damage to the aquatic community over a 1-mile square area.

From the estuary data shown in Table B it may be determined that a quantity of from 0.75 tons to 7.5 tons of a material with a 3 rating in Column VII of the Rating Table would cause death to aquatic organisms within the tidal prism.* It must be noted that this is the effect of a single discharge occurring once within the flushing period under the assumption that no other waste loads or environmental stresses are present. Similar effects would be expected from continuing daily discharges of 40 to 400 pounds of non-degrading materials with a 3 rating in Column VII of Table XI.

---

* Definition -- the volume enclosed within a tidal range in a given estuary upstream of a given point.

Similar analyses coupled with rational judgment can yield much additional useful information, such as that shown below.

Toxic discharge levels which would be expected to kill most aquatic life in specified systems

Material Aquatic Hazard Level	Toxicity Ranges (TL_m) mg/l	Rivers* (1000 cfs)	Estuary*	Shallow* Coastal Waters
1	100-1000	6.6-66 tons	62.5-625 tons	5000-50000 tons
2	10-100	1320-13200 lbs	6.25-62.5 tons	500-5000 tons
3	1-10	132-1320 lbs	0.62-6.25 tons	50-500 tons
4(a)	0.1-1.0	13-132 lbs	125-1250 lbs	5-50 tons
4(b)	0.01-0.1	1.3-13 lbs	12.5-125 lbs	0.5-5 tons
4(c)	<0.01	<1.3 lbs	<12.5 lbs	<0.5 tons

These numbers are presented with some hesitance because of the danger of their being misused or misinterpreted. However, they provide a useful way of displaying the ranges of dangerous discharges and emphasizing the particular effect of very hazardous materials (i.e., those with TL_m values less than 1).

* See examples 1, 2, and 3 in Appendix 1 for assumed system and material characteristics and metric equivalents.

REACTIVITY HAZARD RATINGS

This section deals specifically with those hazards which may result either from contact of the cargo with water or from self-reaction, e.g., polymerization or decomposition. Hazards arising from reaction with other cargoes have been covered by U. S. Coast Guard Publication NVC 5-70 and subsequent revisions, copies of which are available from Commandant, U. S. Coast Guard, Department of Transportation, Washington, D. C. 20590.

Basically, for Coast Guard purposes, a reaction hazard develops when there is a release of energy (heat) and/or of a gas or vapor. The former presents obvious problems; the latter may result in an excessive increase of pressure within the cargo space or occasionally in the release of a toxic or obnoxious cloud. Development of bases for quantitative ratings for reaction hazards of the wide variety of materials involved in water transportation is complex.

Numerous criteria have been proposed for assessing the hazards of systems involving chemical reactions. Among these are such phenomena as (1) Enthalpy of Reaction, (2) Activation Energy, (3) Reaction Kinetics, (4) Thermodynamic Reaction Potential, etc. Some or all of these have been combined into specialized computer programs, but none appears to be pre-eminently suitable for present purposes. Recommendation herein of the empirically based rating system for reactivity hazard ratings does not preclude modifications as developing conditions warrant.

It must be recognized that while the data gathering procedures are empirical, they do supply adequate information upon which to establish a rating system suitable for Coast Guard purposes. Caution is urged in extrapolation of the data beyond its current intent; it must not be considered as a basis for all-purpose classification of the hazards of reactions of chemicals with water or with themselves.

COLUMN VIII - WATER REACTIVITY

In Column VIII the several chemicals are classified on the basis of their tendency to undergo a hazardous reaction when mixed with water. In event the gaseous reaction product (if any) is hazardous per se that fact is noted, but the rating herein is on the reaction alone. It is considered that hazards may arise from (1) a release of sufficient energy to raise cargo temperature, (2) any release of a gas, or (3) a combination of the two. Release of gas of any kind is potentially hazardous when large cargoes are involved, so the degree of hazard is really a function of temperature rise only.

In determining the effects of reaction with water, the test method to be used is that developed for evaluating binary chemical reactions and described in NAS-NRC publication, Compatibility Guide for Adjacent Loading of Bulk Liquid Cargoes, A Report to the Department of Transportation, U. S. Coast Guard, Prepared Under Contract No. DOT-CG-41680-A by the Chemical Reactivity Panel of the Committee on Hazardous Materials, National Academy of Sciences, Washington, DC (Feb. 1975).

Table VIII - WATER REACTION HAZARD RATING

Grade 0	Insignificant Hazard: No reaction with water below 50°C.
Grade 1	Slightly Hazardous: Reaction with water below 50°C resulting in temperature rise of less than 25°C with no gas evolution.
Grade 2	Hazardous Reaction: Reaction with water below 50°C resulting in temperature rise of more than 25°C but less than 50°C with no gas evolution.
Grade 3	Highly Hazardous: Reaction with water below 50°C resulting in temperature rise of less than 50°C with gas evolution or temperature rise greater than 50°C with no gas evolution.
Grade 4	Extremely Hazardous: Reaction with water below 50°C resulting in temperature rise of 50°C or higher with gas evolution.

COLUMN IX - SELF-REACTION HAZARD RATING

In Column IX the chemicals are rated on the basis of their tendency to undergo a hazardous self-reaction, usually polymerization. Ratings of organic chemicals only are significant since the inorganic chemicals presently shipped in bulk do not undergo self-reaction, or polymerization, and hence are rated <u>0</u>. Here, again, energy release and gas evolution can be used as rating criteria, but at the present time quantitative data on activation energy, reaction kinetics, etc., are such that semi-empirical test procedures are recommended for use. The test method to be used has been developed by the American Society for Testing and Materials Committee E-27, "Thermal Instability of Confined Condensed

Phase Systems" (Method E 476-73)*. This method measures the magnitude and rate of heat and pressure generation by the chemical system under test. Gas generation per se is hazardous, so the variations in hazard ratings are primarily on the basis of temperature rises occasioned by exothermic reaction. These criteria are sufficient to meet Coast Guard needs but, again, caution is urged in attempting to extend the ratings to other uses.

Table IX - SELF-REACTION HAZARD RATING

Grade 0	Insignificant Hazard: Exhibits no exotherm under confinement at temperatures under 150°C
Grade 1	Slightly Hazardous: Exhibits an exothermic reaction between 100°C and 150°C but no evolution or generation of gas.
Grade 2	Hazardous: Exhibits an exothermic reaction between 50°C and 100°C with no gas generation, or an exothermic reaction between 100°C and 150°C with gas generation.
Grade 3	Highly Hazardous: Exhibits an exothermic reaction at temperatures below 50°C with no gas generation, or an exothermic reaction at temperatures between 50°C and 100°C with gas generation.
Grade 4	Extremely Hazardous: Exhibits an exothermic reaction at 50°C or less with gas generation.

*Available from American Society for Testing and Materials, 1916 Race Street, Philadelphia, PA 19103

GRADE	I FIRE	II HEALTH Skin and Eyes	III Vapor Inhalation	IV Gas Inhalation	V Repeated Inhalation	VI WATER POLLUTION Human Toxicity	VII Aquatic Toxicity	VIII REACTION Water Reaction	IX Self-Reaction
0	Insignif. Hazard Non-Combust	Insignif. Hazard All not described below	Insignif. Hazard All not described below	Not Applicable	Insignif. Hazard OSHA ≥ 1000 ppm	Insignif. Hazard LD_{50} > 5000 mg/kg	Insignif. Hazard TL_m >1000mg/l	Insignif. Hazard No reaction < 50°C	Insignif. Hazard No reaction <150°C
1	Slightly Hazardous FPcc >140°F (60°C)	Slightly Hazardous Corrosive to eyes	Slightly Hazardous Depressants, Asphyxiants	All those not described below	Slightly Hazardous OSHA 100-1000ppm	Slightly Hazardous LD_{50} 500-5000mg/kg	Practically Nontoxic TL_m 100-1000mg/l	Slightly Hazardous Reaction <50°C ΔT >25°C no gas evolution	Slightly Hazardous Reaction ≥100°C ≤150°C No gas evolution
2	Hazardous FPcc 100°F-140°F (37.8°-60°C)	Moderately Hazardous Corrosive to skin	Moderately Hazardous LC_{50} 200=2000ppm	Moderately Hazardous LC_{50} 200-2000ppm	Moderately Hazardous OSHA 10-100 ppm	Moderately Hazardous LD_{50} 50-500 mg/kg	Slightly Toxic TL_m 10-100 mg/l	Hazardous Reaction <50°C ΔT>25°C <50°C No gas evolution	Hazardous Reaction ≥50°C ≤100°C, no gas evolution, or, reaction ≥100°C ≤150°C, w/gas evolution
3	Highly Hazardous (37.8°C) FPcc <100°F BP >100°F (37.8°C)	Highly Hazardous LD_{50} 20-200mg/kg 24 hr. skin contact	Highly Hazardous LC_{50} 50-200ppm or 0.5-2mg/l	Highly Hazardous LC_{50} 50-200ppm	Highly Hazardous OSHA 1-10ppm	Highly Hazardous LD_{50} 5-50mg/kg	Moderately Toxic TL_m 1-10mg/l	Highly Hazardous Reaction <50°C ΔT>50°C/no gas ΔT<50°C/with gas evolution	Highly Hazardous Reaction <50°C, no gas evolution or, reaction ≥50°C ≤100°C, w/gas evolution
4	Extremely Hazardous (37.8°C) FPcc <100°F BP <100PF (37.8°C)	Extremely Hazardous LD_{50} ≤20mg/kg 24 hr. skin contact	Extremely Hazardous LC_{50} ≤50ppm or ≤ 0.5mg/l	Extremely Hazardous LC_{50} ≤ 50ppm	Extremely Hazardous OSHA <1ppm	Extremely Hazardous LD_{50} < 5mg/kg	Highly Toxic TL_m < 1mg/l	Extremely Hazardous Reaction < 50°C ΔT >50°C/with gas evolation	Extremely Hazardous Reaction <50°C, w/gas evolution

Table X - SUMMARY OF HAZARD CLASSIFICATION CRITERIA

APPENDIX

EXAMPLES OF EVALUATION OF POTENTIAL DISCHARGES INTO SELECTED AQUATIC SYSTEMS*

EXAMPLE I - DISCHARGE INTO COASTAL WATERS

Purpose: To evaluate the range of concentrations which result when a material is discharged in varying quantities into a typical coastal water.

Assumed material characteristics: The material discharged is assumed to be a water soluble substance which is discharged over a relatively short period of time (i.e., one hour) and which mixes vertically within the water column. The material is assumed not to settle out, volatilize, stratify or degrade within the period of time necessary to disperse over a one-square-mile surface area.

Assumed system characteristics: The system chosen is a coastal water with a depth of 60 feet such as would be found approximately 40 miles offshore from two major chemical shipping ports.

*The U.S. units used in this study have the following equivalents:

1 ton (U.S.) = 2000 lbs. = 0.893 long tons - 0.907 metric tons
1 gallon (U.S.) = 0.833 Imperial gallons = 3.785 liters
1 statute mile = 1.6093 kilometers
1 sq. mile = 2.59 sq. kilometers
1 foot = 0.3048 meters

Method of analysis and results: The following Table A presents average concentration which would be found if a given discharge of the material were dispersed over areas 0.25 miles square (1/16 sq. mile); 0.5 miles square (1/4 sq. mile), and 1.0 mile sq. (1.0 sq. miles).

Table A

Concentration of Materials in Coastal Waters

Amount of Material Discharged	Weight of Material Discharged	Resulting Concentration in ppm 1/4 mile sq.	1/2 mile sq.	1 mile sq.
1 pound	1 lb	0.00015	0.00004	---
10 pounds	10 lb	0.0015	0.0004	---
55 gal. drum	458 lb	0.068	0.016	0.004
110 gal. drum	916 lb	0.136	0.032	0.008
1 ton	2000 lb	0.3	0.075	0.019
10 tons	2×10^4 lb	3.0	0.75	0.19
100 tons	2×10^5 lb	30	7.5	1.9
1000 tons	2×10^6 lb	300	75	19
10000 tons	2×10^7 lb	3000	750	190
100000 tons	2×10^8 lb	30000	7500	1900

Weight of 1/2 mile sq. x 60 ft. deep
$= (5280 \text{ ft}/4)^2 \times 60 \text{ ft} \times 64.2 \text{ lb/ft}^3 = 6700 \times 10^6$ lbs
Weight of 1/2 mile sq. x 60 ft. deep = 26800×10^6 lbs
Weight of 1 mile sq. x 60 ft. deep = 107200×10^6 lbs

$$\text{Concentration (ppm)} = \frac{\text{Weight of Material in lbs}}{\text{Weight of water in million lbs}}$$

EXAMPLE II - DISCHARGE INTO AN ESTUARY

Purpose: To evaluate the range of concentrations to be found under short- and long-term conditions of a material discharged in varying quantities into an estuary.

Assumed material characteristics: The material discharged is assumed to be a water soluble substance which is discharged within a single tidal cycle and which mixes uniformly throughout the estuary cross section. The material is assumed to not settle out, volatilize, stratify, or degrade within the tidal cycle period.

Assumed system characteristics: The estuary chosen as the example system is an estuary with an average width of 500 ft., a depth of 40 feet, and length of 15 miles. The estuary is assumed to have an average tidal range of one foot and a flushing time of 40 days. The example analysis point is assumed to lie at the appropriate centers of shipping 7.5 miles from the upper end of the estuary.

Method of analysis and evaluation of results: Two analyses were made and are displayed in Table B. The first is the average concentration which would be expected in the tidal excursion of water passing a discharge point within the tidal cycle. It could either be assumed that the material diffused into this volume or that the discharge occurred during the entire upstream or downstream movement of the water.

The second analysis solves for the average concentration under the assumption that the material from the single discharge remains in the system until it mixes throughout the estuary volume.

Several additional rough assumptions may be made using the above values and the characteristics of this as related systems.

If a uniform discharge were to occur each day of a non-degradable substance as a result of cleaning or loading operations from a single discharge, the cumulative average concentration would be 40 times (i.e., flushing time) the given values for the average concentration throughout the estuary.

If the material discharged daily were to decay at a rate of 0.1 (10%) per day, the resultant concentration would average

$$\frac{\text{(table concentration in ppm)}}{\text{decay rate (i.e., 0.1)}} = \text{approximately 10 times the table concentration}$$

If the decay were as a result of aerobic biological degradation, the oxygen demand in this type of system would be approximately equal to the total ultimate oxygen demand of each day's discharge.

A tidal range of four feet would increase the tidal prism a factor of 4 and decrease the concentrations for the short time concentration by a factor of 4 (or more if increased dispersion occurred).

In an estuary additional factors not considered in this example may become very important.

The concentration of materials which are lighter than water, or which are discharged into the upper layers of stratified systems, may have concentrations higher than those shown. Similarly, heavy materials, or those discharged into the bottom of stratified systems, would tend to have lower initial surface concentrations but may be carried upstream by the saline water wedge for later release into surface layers.

Table B

Concentration of Material in Assumed Estuaries

Amount of Material Discharged	Weight of Material Discharged	Resulting Concentration in ppm	
		In Tidal Excursion	In Total Estuary
1 pound	1 lb	0.0008	0.00001
10 pounds	10 lbs	0.0080	0.0001
55 gal. drum	458 lbs	0.38	0.0046
110 gal. drum	916 lbs	0.76	0.0092
1 ton	2000 lbs	1.6	0.02
10 tons	2×10^4 lbs	16	0.2
100 tons	2×10^5 lbs	160	2.0
1000 tons	2×10^6 lbs	1600	20
10000 tons	2×10^7 lbs	16000	200
100000 tons	2×10^8 lbs	160000	2000

$$\text{Length of Tidal Excursion} = \frac{\text{Tidal Volume above the Point of Analysis}}{\text{Cross Section Area}}$$

$$= \frac{500 \text{ ft.} \times 1 \text{ ft.} \times 7.5 \text{ miles} \times 5280 \text{ ft/mile}}{500 \text{ ft.} \times 40 \text{ ft.}} = 990 \text{ ft.}$$

Weight of Tidal Excursion Water Volume

$$= 990 \text{ ft.} \times 500 \text{ ft.} \times 40 \text{ ft.} \times 63.0 \text{ lb/ft.}^3 = 1247 \times 10^6 \text{ lb.}$$

Weight of Estuary Water Volume

$$= 15 \text{ miles} \times 5280 \text{ ft/mile} \times 500 \text{ ft.} \times 40 \text{ ft.} \times 63.0 \text{ lb/ft}^3$$

$$= 99800 \times 10^6 \text{ lb.}$$

EXAMPLE III - DISCHARGE INTO A FRESHWATER RIVER

Purpose: To evaluate the range of concentrations to be found of a material discharged in varying quantities into a freshwater stream which is used for transportation of hazardous materials.

Assumed material characteristics: The material discharged is assumed to be a water soluble substance which is discharged over a finite period of time (i.e., six hours) and which mixes uniformly throughout the river cross section. The material is assumed not to settle out, volatilize, stratify or materially degrade within the discharge period (i.e., six hours).

Assumed characteristics: A river with streamflows of 1000 and 5000 cubic feet per second (cfs). The lower flow is a typical summer flow found in several inland streams used for navigation and the transportation of hazardous materials. The larger flow is a typical flow found in larger navigable rivers used for deep draft ocean commerce.

The material release time of six hours stated above is chosen to provide for a reasonable time of release of larger cargoes and to provide for reasonable longitudinal mixing.

If the three hour mixing zone were used, the concentrations would be twice the shown values. Similarly, if discharge were over a 12-hour period, the values would be one-half of those given.

Table C

Concentration of Materials in the Assumed River

Amount of Material Discharged	Weight of Material Discharged	Resulting Concentration in ppm	
		1000 cfs River	5000 cfs River
1 pound	1 lb	0.0075	0.0015
10 pounds	10 lb	0.075	0.015
55 gal. drum	458 lb	3.4	0.68
110 gal. drum	916 lb	6.8	1.36
1 ton	2000 lb	15.0	3.0
10 tons	2×10^4 lb	150	30
100 tons	2×10^6 lb	1500	300
1000 tons	2×10^6 lb	15000	3000
10000 tons	2×10^7 lb	150000	30000
100000 tons	2×10^8 lb	NA	300000

Weight of Mixing Volume:

at 1000 cfs: $$100\frac{ft^3}{sec} \times 62.4\frac{lb}{ft^3} \times 6\ hr \times 3600\ \frac{sec}{hr}$$

$$= 135 \times 10^6\ lb$$

5000 cfs: $$5000\frac{ft^3}{sec} \times 62.4\ \frac{lb}{ft^3} \times 6\ hr \times 3600\ \frac{sec}{hr}$$

$$= 675 \times 10^6\ lb$$

BIBLIOGRAPHY

Encyclopedia of Occupational Health and Safety, Two Volumes, International Labour Organization, Geneva, 1972

Fawcett, H. H., Toxicity vs. Hazard, pages 279-289, and Foulger, J. H., Effect of Toxic Agents, pages 250-278, in Fawcett and Wood, Safety and Accident Prevention in Chemical Operations, Interscience, Wiley, New York, 1965

Fire Protection Guide on Hazardous Materials, Fourth Edition; Flash Point Index of Trade Name Liquids 1972; National Fire Protection Association, 470 Atlantic Avenue, Boston, Mass. 02210

Flash Points, The British Drug Houses, Ltd., Poole, England, 1963

Murphy, Sheldon D., The Toxicity of Pesticides and Their Metabolites pages 313-335, in Degradation of Synthetic Organic Molecules in the Biosphere -- Natural, Pesticidal, and Various Other Man-Made Compounds, Proceedings of a Conference, San Francisco, California June 12-13, 1971, Committee on Agriculture and the Environment, ISBN 0=309-02046-8, National Academy of Sciences, 2101 Constitution Avenue, N.W., Washington, D.C. 20418, 1972

Patty, F., Industrial Hygiene and Toxicology, Two Volumes, Second Edition, Interscience, Wiley, 1967

Spector, W. S., Handbook of Toxicology, Volume I, National Academy of Sciences, Washington, D. C. 1956

Water Quality Criteria Data Book, Volume I - Organic Chemical Pollution of Freshwater, December 1970, Environmental Protection Agency, Water Quality Office: for sale by Superintendent of Documents, Government Printing Office, Washington, D.C., 20402, Catalog No. EP2.10:18010 DPV 12/70/v.1, Price 3.50

Water Quality Criteria Data Book, Volume II - Inorganic Chemical Pollution of Freshwater, July 1971. Environmental Protection Agency; for sale by the Superintendent of Documents, Government Printing Office, Washington, D. C. 20402, Catalog No. EP1.16: 18010 DPV 07/71/v.2, Price 2.25

Water Quality Criteria Data Book, Volume III - Effects of Chemicals on Aquatic Life, May 1971, Environmental Protection Agency; for sale by the Superintendent of Documents, Government Printing Office, Washington, D. C. 20402, Catalog No. EP1.16:18050 GWV 05/71/v.3, Price 3.75

Water Quality Criteria Data Book, Volume IV - An Investigation into Recreational Water Quality, April 1972, Office of Research & Monitoring, U. S. Environmental Protection Agency, Washington, D. C. 20460; for sale by U. S. Government Printing Office at some future date from February 1973.