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Interpretation of Chemical Water Quality Data

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ABSTRACT: Meaningful interpretation of water quality data requires an evaluation of the reliability of the data. Particular attention must be given to evaluation of the applicability of the analytical methods used, sampling and sample handling procedures, and analytical quality control program.

There are many problems with the use of the U.S. Environmental Protection Agency (EPA) water quality criteria as a basis for evaluating water quality. Meaningful interpretation of data requires consideration of the concentration-time of the exposure relationships that exist at a given location within a body of water where the concentration of a chemical is in excess of the U.S. EPA criterion. Also, consideration must be given to the amount of the contaminant which is available to affect water quality. This may require the use of bioassay procedures since, in general, chemical procedures provide a relatively poor estimate of the amount of available contaminant present in a water sample. In addition, consideration must be given to the physical and chemical characteristics of the water since they may markedly affect the significance of a chemical contaminant for water quality.

KEY WORDS: water quality, data interpretation, water quality criteria, aquatic toxicology

In the past, water quality has been judged primarily on the basis of parameters such as biochemical oxygen demand (BOD), suspended solids, and other gross pollutional characteristics. However, as a result of the development of water quality criteria for a large number of potentially hazardous chemicals, increasing emphasis is being placed on the critical concentrations of trace contaminants in natural waters as indicators of water quality. The U.S. Environmental Protection Agency (EPA) *Quality Criteria for Water* [*1*],[2] published in July 1976, presents criteria for approximately 50 chemical parameters or characteristics of water. By 30

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[2]The italic numbers in brackets refer to the list of references appended to this paper.

June 1978, the EPA, in accord with the Consent Decree arising from the environmental activists' lawsuit concerning the control of hazardous chemicals, must promulgate water quality criteria for approximately 50 additional compounds. Therefore, in the near future, the critical concentrations for a total of approximately 100 chemicals will be available for use as the basis for judging water quality, in which the criteria will be compared with the results of chemical analyses of natural waters.

Whereas most of the papers presented at this symposium have been devoted to research leading to the development of water quality criteria, this paper presents a discussion of the utilization of these criteria for water quality management purposes. Included in this discussion is guidance for the evaluation of data reliability and interpretation with respect to water quality.

Evaluation of Reliability of Water Quality Data

There are two aspects of the interpretation of chemical data with respect to water quality. The first and most frequently overlooked aspect is the evaluation of the quality of the data which serve as the basis for comparison with the water quality criteria. The second phase is the proper evaluation of the reliable chemical data relative to the water quality criteria. Both of these aspects are discussed below.

Analytical Methods

The first and most important step in any utilization of chemical data for assessing the significance to water quality of a particular analytical result, is an evaluation of the reliability of the data. Far too often, this phase of the study is glossed over or ignored. It is the experience of the authors that frequently little credibility can be ascribed to chemical data resulting from the analysis, by analytical laboratories performing routine water analyses, of samples containing concentrations of contaminants at or near the critical levels promulgated by the U.S. EPA in July 1976. There are several reasons for this. More times than not, the "standard methods" procedures such as the *Standard Methods for the Examination of Water and Wastewater* [*2*] by the American Public Health Association (APHA) and others, the American Society for Testing and Materials' *Annual Book of ASTM Standards* [*3*], or the U.S. EPA's *Methods for Chemical Analysis of Water and Wastes* [*4*] are used without evaluating the applicability of the particular analytical procedures to the water being investigated. Many analysts assume that because the U.S. EPA, ASTM, or the American Public Health Association (APHA), American Water Works Association (AWWA), and Water Pollution Control Federation (WPCF) developed an analytical procedure and put it in a standard methods manual, this

method can be used without evaluating its reliability. Anyone who is involved in the development of standard methods of analyses knows that each time a new edition of a manual is developed, some of the procedures are modified. These modifications hopefully improve the reliability of the procedure, although this has not always proven to be the case.

Several years ago, Lee [5] discussed the "standard methods syndrome" in which he pointed out the fallacy of the commonly held view that various laboratories utilizing the same analytical procedures will obtain comparable results. As discussed by Lee, the primary problem with standardized methods or other analytical procedures yielding comparable results, is the presence of substances in a water sample which interfere with the analysis. These interferences are particularly significant when the concentrations of the contaminant(s) of interest are at low levels (μg/litre), such as those which are now being found to be adverse to the reproduction of aquatic life. The same analytical procedure may not yield comparable results over the same year for a particular body of water because of changes in the concentrations of interfering substances that occur at various times. Analytical procedures have to be checked at frequent intervals to ensure that they are applicable to the water that is being analyzed. Failure to do this, especially at μg/litre concentration levels, can readily result in the production of a large amount of essentially meaningless data.

Another reason for the relatively poor reliability of the results of most chemical analyses of samples with concentrations of contaminants of interest at or near μg/litre levels, is the assumption that analytical procedures which work well at the mg/litre levels can be readily modified for analysis at μg/litre levels. Most water and wastewater analysis laboratories usually determine concentrations of contaminants at mg/litre or tenths of a mg/litre levels. Examination of the July 1976 *Quality Criteria for Water* shows that the critical concentrations of many contaminants of particular interest are on the order of ten or less μg/litre. Frequently, these critical levels are one to three orders of magnitude lower than the level routinely determined by water analysis laboratories. There may be a legal requirement that one of the "standard methods" be used by a laboratory, but usually this legal requirement allows for the use of an "appropriate equivalent" analytical method. The legal requirement never, to the knowledge of the authors, requires that a method be used for the analysis of a sample when the method does not provide reliable analytical results.

Sampling and Sample Handling

Evaluation of the reliability of the chemical data based on the analysis of natural waters should consider not only the reliability of the analytical methods used but also the methods of sample collection and handling. A review of laboratory practices will show that many water and wastewater analysis laboratories must let samples stand for periods of weeks to some-

times months before analysis because they cannot readily handle the numbers of samples provided to them. For many chemical constituents, in which there is interest in a specific chemical form, the analyses have to be done almost immediately after the sample collection. It is rare that samples can be stored for any period of time without significant alteration of the chemical species present. The methods of handling and storage may even make the results of the analysis for the total content for a particular chemical invalid. This situation has been found in association with freezing during storage of some lake water samples on which analyses of total phosphate were to be made. Evidently, the freezing process concentrates the solutes, which leads to the precipitation of hydroxyapatite, some of which will not redissolve even with strong acidification.

The authors have also experienced the situation in which a state pollution control agency conducted a year-long study of a number of bodies of water, in which they sampled at periodic intervals and measured a number of parameters. Examination of the data showed that the values for a number of the parameters all changed markedly at one point during the study. Since the directions and magnitudes of the changes were not typical for natural waters of the type being studied, questions were asked about what took place which could have caused this change. It was found that at that time the state agency had changed the laboratories doing the chemical analyses. Although both analytical laboratories were using the same analytical procedures, one of the laboratories, because of its workload, allowed the samples to stand from one to two months before analyses could be performed on them. The other laboratory was able to analyze the samples within a week of receipt. This difference in handling changed the concentrations of certain parameters by an order of magnitude. This finding completely invalidated the study since some of the key parameters in the study were those that changed with the change in analytical laboratories.

Lee [*6*] has discussed many of the problems associated with the chemical analysis of natural waters. As discussed by Lee, one should not automatically assume that the "standard methods procedures" for sample preservation are reliable. Sometimes methods appear in "standard methods" without proper review by the analytical community. A method found to work satisfactorily in one laboratory may not have been properly evaluated in a wide variety of laboratories or for the variety of waters for which the method may be used. This is especially true for the *Standard Methods for the Examination of Water and Wastewater* [*2*] by the APHA and others, where the analytical procedures are frequently not subjected to any round-robin testing prior to adoption. Even with round-robin testing, such as is used for the ASTM procedures, it is rare that the methods of sample collection, preservation, and handling are tested. Usually the testing is restricted to an ampule sample prepared by a central laboratory, which is to be diluted upon receipt to some known volume and then analyzed.

It is generally necessary to conduct studies to determine the appropri-

ateness of sample collection and handling procedures. The first time that a particular water is sampled, additional samples should be collected to ensure that the sampling method does not bias the results of the analysis, that the sample locations are representative of the waters studied, and that the proposed methods of sample storage and handling are adequate to maintain the integrity of the samples with respect to the parameters of interest. If at any time the characteristics of the body of water, such as the flow in a river, the addition or removal of municipal or industrial wastes from upstream sources, or the temperature (that is, from winter to summer) change significantly, additional work should be done to establish the appropriateness and reliability of the sample collection and handling techniques.

In reviewing data for use in water quality evaluation, one should inquire into the methods that were used for sample collection and handling and then make a judgement as to the adequacy of these methods in light of the intended use of the data. A note of caution should be made in connection with using data from previous investigations. Often, investigators will collect and use data for a specific purpose. The reviewer who is attempting to use the data at a later time for a different purpose must be certain that the data were collected in such a way that they can be made useful for his objectives.

A common misconception exists in the water analysis field with respect to the use of "historical data." It is often inappropriate, in modern-day studies, to use outdated procedures that may have been used in previous studies in order to provide a common basis of comparison between current and past data. This approach can be used if the investigator is certain that the method used does not invalidate the results of the previous analyses of the body of water and that the interfering substances in the body of water have not changed so as to render the method inappropriate for use today. This will rarely be possible, however, for waters that are impacted by human activity.

Quality Control Program

The key to the evaluation of the reliability of the results of chemical analyses is an examination of the laboratory's quality control program and the results of quality control tests for the analyses of interest. In 1972, the U.S. EPA provided a detailed guide for analytical quality control for water analysis [7]. Even though this manual has been out for a number of years, there are still some, and quite possibly many, water analysis laboratories that are not following the procedures outlined in this manual. In addition to the guidance for analytical quality control provided in the U.S. EPA manual, the *Standard Methods for the Examination of Water and Wastewater* [2], by the APHA and others, and a number of other

manuals and specialized books provide guidance to the development of analytical quality control programs which can be used in routine water analysis laboratories.

There is often considerable reluctance on the part of some directors of routine water analysis laboratories to adopt adequate quality control programs. This reluctance stems from the fact that an adequate quality control program greatly cuts back on the number of samples that can be processed since additional samples (that is, standard samples, spiked samples, replicates, etc.) must be analyzed. The U.S. EPA *Handbook* [7] provides guidance on the number of replicate, spiked, and standard samples that should be run. Every water analysis laboratory should follow this approach, especially those that are analyzing a wide variety of samples from different sources. In a situation in which analysis is made of a group of samples of essentially the same character, collected in one area over a short time span, it is possible to cut back on the number of replicate samples since there is a form of replication created by the closely spaced sampling.

It is important that laboratories check not only the reproducibility of their analytical techniques but also the reproducibility associated with the overall sampling and handling procedure. As a standard part of any quality control program, samples should be split at the time of collection into a series of identical subsamples. These should be analyzed as though they were individual samples. Also, a number of replicate samples should be collected and analyzed. The results of these analyses should be presented in any laboratory report and summarized in the publication of the data. This will give the user of the data the opportunity to judge the adequacy of the overall sampling and handling program as well as the precision of the analytical methods used.

It should be emphasized that any single quality control parameter does not detect all errors that may occur in an analytical procedure. For example, the recovery of the spike does not necessarily indicate that the analytical procedure is reliable. Interferences in the water could cause the analysis of the original contaminant level to be incorrect and still not interfere significantly with the spike recovery, especially if the spike is large compared with the background levels. It is important that the spike additions be such that resulting concentrations in the spiked sample are just detectable above the ambient level. The entire suite of quality control measures should be used to ensure that the procedures yield reliable data.

The importance of an adequate quality control program, especially when the analysis is for contaminants at the μg/litre level, cannot be overstressed. Routine analysis at these levels is often difficult. This is especially true if the laboratory must analyze samples that range in concentration from mg/litre levels, such as those typically associated with municipal or industrial waste, to the μg/litre levels, or less, associated with natural water systems. It should never be assumed that because a water analysis

laboratory can analyze, with a high degree of precision and accuracy, standard samples provided by a state agency where the concentration ranges supplied are typical of those of municipal and industrial wastes, the laboratory has the same capabilities in performing analyses on typical natural water samples.

Every reviewer of chemical data for natural water samples should request to see the results of the quality control program. Particular attention should be given to the values for each replicate sample as well as the average values, spike recovery, and the precision and accuracy of replicate analyses of standard samples. It is only with this type of information that a data reviewer can begin to judge the adequacy of the analytical program.

It is the experience of the authors that it is generally best to approach any data set skeptically; the reliability of the data must be demonstrated by careful review of the data before it is used. This is especially true for data in which the concentrations of contaminants are reported to be at or near critical levels which cause chronic toxicity or excessive bioconcentration.

Some governmental agencies, industry, and others use contract analytical services in which a commercial or some other laboratory, not under the direct supervision of the data user, performs the analyses. Under these conditions, it is very important for those responsible for establishing the working arrangement with the "contract laboratory" to ensure that the work that is done is of adequate accuracy and precision. It is recommended that those who are responsible for large amounts of contract studies set up their own quality control program in which they prepare replicate samples, spiked samples, and known samples and send these as part of the standard sample set to the contract laboratory in such a way that the contract laboratory is not aware that these samples are part of a quality control program.

The contract must clearly identify the levels of accuracy and precision that must be attained on both the contract laboratory's quality assurance program and the contractor's quality assurance program in order to fulfill the terms of the contract. Further, a mechanism should be established whereby if a firm or the contract laboratory does not satisfactorily conform to the terms of the contract for the first few sets of analyses, the contract may be terminated by the contractor. This latter clause is extremely important in preventing the situation of a laboratory being awarded a contract but producing essentially worthless data because it could not perform the analyses in accord with the required precision and accuracy. The contracting agency should have the power to terminate an analytical contract on short-term notice if the laboratory fails to meet contract specifications for the analyses. It should be noted that these provisions of an adequate quality control program by both the contract laboratory and the con-

tractor will significantly increase the cost of water analysis for many water quality programs over what program managers have been used to paying in the past. However, it is far better to have less data of a known and required degree of reliability than a large amount of essentially worthless data.

There is an aspect of contract analytical arrangements which tends to promote the production of analytical data of poor quality; that is the competitive bid system. A competitive bid arrangement for the award of analytical service contracts, where the contract is normally awarded to the low bidder, tends to work against the production of reliable analytical results for low levels of contaminants. The authors have recently encountered a situation in which they found, as a result of working with a governmental agency contracting for several hundred thousand dollars per year of analytical services, that the firm that was awarded the analytical contract had bid the work at a cost to the agency that was a factor of five less than the cost normally associated with performing the analyses with the specified and required precision and accuracy. It was obvious that since this laboratory was claiming the ability to do this work at a much lower price than the authors had found any other laboratory charging for reliable work, the contract laboratory was probably not performing the analyses with the required precision and accuracy. A review of the data produced by this laboratory showed this to be the case and that the concentrations for some of the heavy metals being reported by this laboratory were a factor of 10 above what would have been expected for the types of waters being examined and above those concentrations found in the same waters in an independent study. The development of a series of spiked samples sent to the contract laboratory showed that this laboratory's analytical results were unreliable for a number of parameters.

Those responsible for establishing working relationships with contract laboratories should carefully check to be certain that the commercial or other laboratories doing work of this type on a contract basis are bidding the analyses at a price which is reasonable and necessary for achieving a high degree of precision and accuracy. Any laboratory that grossly underbids for heavy metals, pesticides, or other analyses of this type at μg/litre levels or less will probably not be able to perform the analyses properly. There is a certain minimum cost necessary for any analysis of this type, and the costs do not vary greatly from laboratory to laboratory. Any contractor who selects a contract analytical laboratory based primarily on the low bid price, when it is considerably lower than that required to do the analyses according to specifications, is likely to find that the data produced will be of limited value in determining the water quality of the area being investigated.

It should be stressed that the authors are skeptical about the overall quality of the work that is being done by both public and private water

analysis laboratories. Discussing these matters with the directors of laboratories often shows that the director is fully aware of these problems but has been forced to adopt short-cut procedures as a result of inadequate support for the work load that his laboratory is required to handle. The fault usually lies not with the laboratory director, but with those responsible for managing the overall appropriations for the laboratory and the study. Laboratory directors are at fault in many instances because they agree to do work under conditions in which they know that the quality of the work may not be adequate to meet the needs of the study. In general, those responsible for supervising or performing the analyses should be more intimately involved in the overall water quality study planning and, especially, the data interpretation. Frequently, those in the laboratory can see significant problems with the analysis of particular sets of samples. The results of these analyses, however, generally show up on a data sheet, with the problems encountered never being brought to light.

Internal Consistency of Data

One of the techniques, which those experienced in water quality data analysis can use to check on the adequacy of a particular analytical program, is the examination of the internal consistency of the data. It is rare that a sample is analyzed for a single parameter. An examination of chemical water quality data usually shows that various parameters change in relation to each other and to certain physical phenomena such as flow, temperature, etc., in a certain, fairly well-defined manner. Those familiar with water quality data generally find that the behavior of conservative chemicals, such as chloride and sodium, and, for waters which do not precipitate calcium carbonate, specific conductance are good indicators of the behavior of some contaminants. In marine waters, temperature and especially salinity are very important factors in determining the movement and distribution of chemical contaminants in natural waters. Further, changes in the oxidation conditions of the water (such as changes from oxic to anoxic) or changes in suspended solid content can cause various parameters to change in fairly well-defined directions. Often the magnitude of change can be readily estimated, based on the normal, expected environmental chemistry of various contaminants in natural water systems. Everyone who uses chemical data for water quality purposes should examine the data as a whole to see that the parameters change in the right direction in relation to changes in the overall characteristics of the water. Individuals with limited experience in this area can readily gain experience through critical examination of the data. Frequently spurious data can be detected in this way or by examination of the time sequence or depth sequence of the data.

Reliability of EPA Criteria

One of the first steps in using water quality criteria in assessing the significance of certain concentrations of chemical contaminants in a water is to examine the reliability of the criteria. An examination of the various drafts of the U.S. EPA water quality criteria shows that a number of rather drastic changes have been made in the draft criteria with little new information or technical justification. The National Academy of Sciences and the National Academy of Engineering (NAS-NAE) developed the *Water Quality Criteria* of 1972 [*8*] (Blue Book). These criteria represent the efforts of approximately 200 scientists and engineers over a several-year period. They were extensively reviewed by the technical community prior to release. As required by PL 92-500, the U.S. EPA developed water quality criteria for a variety of particularly significant chemicals and parameters, the first version of which was issued in Oct. 1973. These criteria were essentially the same as the National Academies' Blue Book values. The second version of the EPA criteria, which became the July 1976 *Quality Criteria for Water* [*1*] (Red Book), was markedly different from the Oct. 1973 version. In some cases, a completely different approach was used for establishing a criterion than was used for the Blue Book values, without any significant addition of new technical literature which would justify such a drastic change. The July 1976 version still contains a number of what might be classified as "drastically changed criteria," changed from the Blue Book values.

There is considerable controversy in the technical community about the reliability of some of the criteria in the Red Book. The American Fisheries Society has taken it upon themselves to conduct a critical review of the Red Book criteria. This review, which is expected to be published in the near future, will show that there are problems with some of the criteria developed by the U.S. EPA. The current efforts of the U.S. EPA to develop water quality criteria for the "consent agreement" list of 65 hazardous chemicals is being extensively reviewed by industry, consulting groups, and university personnel. A good example of the lack of general applicability of some of the U.S. EPA water quality criteria is provided by the current situation in relation to the polychlorinated biphenyl (PCB) criterion. Those associated with PCB studies in the Great Lakes region feel that the current 1 ng/litre criterion set forth by the U.S. EPA in their July 1976 Red Book is too lenient, while those working in other parts of the country, particularly the Gulf Coast and the New York Bight, and others who have had a chance to examine the PCB content of water and fish, find that this criterion is too strict. The problem seems to center on the attempt to apply bioconcentration factors developed in studies on the upper Great Lakes to many other waters of the United States.

A wide variety of natural waters near urban centers in the United States

have been found to contain PCBs in concentrations far in excess of the U.S. EPA 1 ng/litre criterion. Yet, fish and other organisms taken from these areas have concentrations of PCBs within their flesh which are considerably less than the U.S. Food and Drug Administration (FDA) limit of two parts per million in fish flesh used as human food. Since the PCB criterion is based on bioconcentration and the potential hazard to man of consuming excessive amounts of PCBs in his food, there appears to be some problem in applying the 1 ng/litre criterion to those waters where concentrations in fish flesh are well below the FDA limit. It appears, as might be expected for PCBs, that a significant part of the total PCB content of a water which contains large amounts of particulate matter in the form of detritus and/or clastic materials, suspended sediment, etc., is attached firmly enough to the solid phase so that aquatic organisms, for example, fish, are not able to extract the PCBs. The current work on bioconcentration of chemicals such as the chlorinated hydrocarbons is, in general, showing that the very high bioaccumulation of compounds such as PCBs can be achieved by direct uptake from the water. In fact, it appears (see the other papers of this volume) that the food-chain uptake by fish is only a small part of the total uptake. Therefore, suspended sediments would be expected to play a significant role in preventing PCB uptake by aquatic organisms.

A more effective mechanism must be established whereby a review of the new EPA proposed criteria can be made by a group such as the National Academies to ensure that any criteria that are promulgated by the EPA are in accord with the best technical information available at the time of promulgation. Such a group should become a permanent body through which the EPA could maintain a more or less continuous review of the literature. When the EPA feels that it has a sufficient amount of reliable information to justify a criterion, the proposed criterion should be submitted to the established group for review prior to promulgation.

The importance of having reliable water quality criteria cannot be overstressed. The U.S. Congress has recently reaffirmed the basic approach of PL 92-500. It relaxed the general requirements for municipal discharges and some industrial discharges, and placed greater emphasis on a case-by-case approach where the characteristics of the receiving waters must be considered as part of the implementation of the best available treatment of these wastewaters. There was no relaxation, however, of the implementation of the control programs for toxic chemicals. It is extremely important that any water quality control program based on "excessive" concentrations of chemicals in natural waters, as judged by the values exceeding the water quality criteria, be technically valid. The adoption of unrealistic criteria as water quality standards could cause the expenditure of very large amounts of funds in the name of water pollution control with little or no impact on water quality.

The U.S. EPA plans to revise the Red Book criteria and add some water quality criteria for additional hazardous materials. It is expected that draft criteria will be developed which will be made available to the public for comment. Based on past experience with the Red Book criteria of July 1976, it is likely that the U.S. EPA may not adopt all of the technically valid changes that should be made in the criteria, based on the reviewers' comments. Anyone attempting to utilize the current or soon-to-be-released U.S. EPA criteria governing water quality should obtain the reviewers' comments from the EPA if there is any question about the applicability of these criteria to a particular situation. An extensive discussion of the applicability of the U.S. EPA criteria for water quality for use as the basis for developing water quality standards has been presented by Lee and Jones [*9*]. In addition, reviews of various drafts of the U.S. EPA water quality criteria have been prepared by Lee et al [*10*] and by Lee [*11*]. These reviews should be consulted for further information on the problems associated with utilization of the water quality criteria as a basis for judging water quality.

Analytical Chemistry Problems

Some of the critical concentrations listed in the July 1976 U.S. EPA *Quality Criteria for Water* [*1*] are below the reliable detection limit for the analytical procedures that are normally available for use. This is true for PCBs, cyanide, aqueous chlorine, and a number of other chemical species. Laboratories will have to try to extend the capabilities of the currently used analytical procedures down to these levels. For a number of these contaminants, the analytical procedure is reliable at levels an order of magnitude higher than the established criteria. Trying to extend these procedures to levels that are near the criteria will probably be met with great difficulties.

There is another significant problem with utilizing standard analytical procedures to obtain chemical data which are to be used in conjunction with water quality criteria for assessing water quality. This is the fact that the standard chemical tests for some parameters measure only the total concentration of a group of chemical species with similar properties rather than the concentration of a selected component species. An example of this situation is the procedure for toxaphene. Toxaphene consists of a mixture of chlorinated camphene compounds which, in the normally-used analytical procedure, are all lumped together as a single compound. Lee et al [*12*] have shown that the more toxic components of toxaphene tend to degrade rapidly in the environment, leaving a measurable residue which is less toxic than the parent compound.

Another chemical which falls into this category is the anionic surfactant linear alkylbenzene sulfonate (LAS), which is measured by the methylene

blue active substance test (MBAS). This test involves the interactions between the anionic surfactant and the cationic methylene blue dye. The length of the carbon chains in LAS has a significant effect on its toxicity to aquatic life [*13*]. In general, for the same time of exposure, there is a decrease in toxicity to various aquatic species with a decrease in carbon chain length in the C-10 to C-16 range. However, LAS compounds degrade at a fairly rapid rate in the environment and in waste treatment processes, with the longer, more toxic chain-length compounds tending to degrade more rapidly than shorter chain-length compounds. Since shortening the chain length, in general, does not significantly affect the interaction between the methylene blue dye and the LAS, shortening the chain length does not result in a significant decrease in measurable methylene blue active substances. There is, however, a very significant decrease in toxicity to aquatic life associated with partial degradation. There is a problem centered around the fact that the criterion and some states' standards for LAS are expressed in terms of MBAS. These critical values for MBAS are based on fresh, undegraded (that is, longer-chain) LAS. An equal amount of MBAS, as measured in the effluent of a domestic wastewater treatment plant or in a natural water system, however, will be much less toxic (that is, lower in toxicity per unit of methylene blue activity) because of the rapid LAS degradation.

Any user of water quality criteria or standards must examine the characteristics of the analytical procedure used to be certain that it measures the actual chemical species that was the basis for the toxicity data upon which the water quality criterion was developed.

Concentration–Time-of-Exposure Relationship

One of the most important problems associated with trying to use chemical data as a means of judging water quality, based on the U.S. EPA water quality criteria of July 1976, is that these criteria were based on and designed for chronic exposure situations. This type of exposure generally implies exposure during the entire life cycle of an organism or during critical life stages, especially reproduction phases, of an organism. There is little difficulty in interpreting the significance of a concentration of an available form of a contaminant which exceeds the critical concentrations on a continuous basis. Significant problems develop, however, when attempts are made to utilize the EPA criteria for situations in which organisms are exposed to excessive concentrations for periods of time much less than those used in developing the water quality criteria.

It is well known that there is an intimate coupling of the critical concentration of chemicals with the time of organism exposure. For many chemicals, very large concentrations can be present in the aquatic environment of an organism, provided that the time of exposure is short. As the

time of exposure increases, the concentration which has a significant adverse effect on the organism is reduced until it reaches a value of or near the U.S. EPA quality criterion for water. This level is the chronic or safe level for continuous exposure of the organism to the available form of a chemical. Taking a water sample from a river, lake, estuary, or the ocean and finding that the concentration of a contaminant exceeds the U.S. EPA criterion tells one essentially nothing about the potential hazard to the aquatic organisms present in the region from which the sample was taken. In order to interpret data of this type, chemical analyses on a series of water and organism samples over a considerable period of time are needed in order to determine the shape of the concentration-time-of-exposure curve for the contaminant of interest. It is rare that the concentration of a contaminant in a natural water remains at a steady, unvariable value. It has been found for many chemicals that there are periods of time when the concentration will exceed the U.S. EPA criterion of July 1976. There are also periods of time when the levels are less than this value. The potential impact of a situation of this type on aquatic organisms, in which the organisms are exposed to concentrations above the U.S. EPA criteria for short periods of time, is essentially unknown today.

Although the 96-h acute lethal level and the chronic safe-exposure level are known for some chemicals, essentially nothing is known about the critical time-concentration relationship for exposures of less than 96 h or between 96 h and continuous exposure time. It is likely that the concentrations of available forms of some chemical contaminants can exceed the U.S. EPA chronic exposure critical level for periods of months without having a significant adverse effect on the aquatic ecosystem during certain times of the year. At other times, however, exceeding the critical concentrations for a few days to a few weeks may be excessive, especially during the reproductive phases, for certain organisms. This is an area that needs considerable attention at this time. It is clear that the evaluation of the significance of the presence of a particular level of chemical contaminant in natural waters must be based on the concentration-time-of-exposure relationships for that chemical and water. Water quality criteria which are based on matching the time-concentration relationship that exists in a particular body of water must be used to judge the significance of finding a contaminant in excess of the U.S. EPA Red Book criterion.

There are a number of situations in which the U.S. EPA Red Book criteria should not be used. One of these is in the mixing zone associated with municipal or industrial wastewater discharges. The U.S. EPA 1976 *Quality Criteria for Water* [*1*] states that a mixing zone is a zone in which some damage to the ecosystem may take place because of elevated concentrations. As discussed by Lee and Jones [*9*], while damage may occur in this region, it does not necessarily occur. Elevated concentrations in a mixing zone often do not have detrimental effects on aquatic organisms

because of the fact that there is limited likelihood that organisms in a water column can receive a detrimental exposure. Most water column organisms in such an area tend to move through the mixing zone and, therefore, encounter elevated concentrations only for short periods of time.

The exception to this may be with benthic organisms. In general, however, many benthic organisms are relatively insensitive to chemical contaminants. There is so little known about the critical concentrations of chemicals for benthic or epibenthic organisms that one cannot be certain that even an excessive concentration, based on U.S. EPA criteria for chronic exposure to a water-column organism such as a zooplankter or fish, is necessarily adverse to benthic organisms. Before any application of the July 1976 criteria is made to benthic organisms, studies must be done to ascertain whether or not these criteria, which were, in general, based on studies of zooplankton or fish, have general applicability to benthics as well. It is important, therefore, that one not automatically assume that some significant adverse effect would occur in a mixing zone of a municipal or industrial waste outfall only because the concentrations of some contaminants exceed the Red Book values.

Another situation in which the U.S. EPA July 1976 criteria should not be used is that of intermittent discharges. A prime example of a significant error on the part of the U.S. EPA in developing water pollution regulations occurred in the 11 Jan. 1977 *Federal Register* [*14*] governing ocean dumping of dredged sediment. It is specified in this regulation that the July 1976 Red Book criteria shall be used to judge the significance of chemical contaminants present at the edge of a mixing zone associated with ocean-dumped dredged sediment. Since the ocean dumping of dredged sediment is an intermittent process in which dumping usually takes place every hour or so, and since this dumping takes place in a zone of relatively high mixing in open waters, it is virtually impossible for the dumping to create a situation in which an organism in the water column would receive a dose of a chemical contaminant in excess of the critical time-concentration levels. Hopefully, these regulations will be changed in the near future to reflect more properly the current understanding of the concentration-time-of-exposure relationship associated with ocean dumping of dredged sediments.

Available Forms of Contaminants

The authors feel that one of the most significant deficiencies of the EPA water quality criteria promulgated in July 1976 is that they generally specify total contaminant levels. Many chemicals exist in natural waters in a wide variety of forms, only a limited number of which are available to affect aquatic life or water quality. As discussed by Lee [*15*], far too often the chemical environment associated with a bioassay test that is used to establish a water quality criterion is not properly defined. Further, it can

be expected that many times the general chemical environment that exists in a particular natural water is markedly different from the environment that was present in the toxicity test that was used to establish the water quality criterion. In reviewing chemical data with respect to water quality in a specific area, consideration must be given to the relationship between the chemical environment of the bioassay test and the chemical environment that exists in the waters under investigation. As discussed by Lee [*15*], a review of a chemical environment must consider the oxidation state, complexes, solubility, sorption, precipitates and other particulate forms, and so forth, to be certain that what appears to be an excessive concentration of a chemical contaminant is in fact an excessive concentration of available forms. Failure to consider this relationship properly could easily result in a situation in which what would be judged to be an excessive concentration of a contaminant, based on the July 1976 EPA criterion, would in reality be a safe concentration. Further, one must consider not only the chemical species actually present in a water at the time of sampling but also future conditions that could alter the availability, to aquatic organisms, of the chemical contaminant in the water. An important question to consider is, can a chemical present in an unavailable form today be converted to a form at some time in the future so that the concentration would have a detrimental effect on aquatic life? The assessment of this situation requires an understanding of the aqueous environmental chemistry of the chemical.

Progress is being made today in modeling the behavior of contaminants in natural water. Through the use of deterministic models, such as those being developed in the E35.21.02 section, devoted to environmental chemistry-fate modeling, of Committee E-35 on Pesticides of the American Society for Testing and Materials, it will be possible to determine whether or not what appears to be a safe situation now, will, at some time in the future, because of transformations of the forms of the contaminant, create an adverse condition for aquatic life.

At the present time, the bioassays used for determining the critical concentrations are usually conducted with what are considered to be the most available chemical forms, such as the aquospecies for heavy metals. Rarely has work been done with complexes, particulate forms, different oxidation states, sorbed species, etc. This is an area that needs considerable research at this time if the July 1976 U.S. EPA water quality criteria are to be used in a meaningful way to judge the significance of a concentration of a particular contaminant in natural water.

One of the reasons why the National Academies' Blue Book panel chose to use the acute lethal test with an application factor designed to relate acute lethal to chronic safe levels is that factors such as hardness, alkalinity, total salts, and other bulk characteristics of the water affect the toxicity of many chemicals. A comparison between the National Academies' Blue

Book and the U.S. EPA's Red Book shows that in developing the Red Book criteria, the U.S. EPA has often not followed the National Academies' Blue Book recommendations of adopting water quality criteria based on bioassay procedures and an application factor rather than on chemical analyses. While the EPA has retained a 96-h bioassay application factor approach for some chemical species, it has eliminated them for many that were recommended by the Blue Book criteria review panels. While there is no doubt that the chemical approach is administratively more simple, it is certainly not more technically valid. Many of the National Academies' advisory panels concluded that there are enough different factors affecting the toxicity of a particular chemical residue to make it essentially impossible to determine toxicity based on chemical tests. Further, there are a number of analytical constraints for many compounds (which are discussed in a previous section) which make the bioassay procedure a much more appropriate one for assessing effects on water quality. In reviewing these criteria with respect to the results of the chemical analyses, consideration must be given to whether the general characteristics of the water, such as hardness, alkalinity, and total salts are such as to significantly affect the toxicity in a particular water. In many instances, it may be necessary to utilize a bioassay test to check on the appropriateness of the July 1976 criteria. It is almost certain that as the U.S. EPA water quality criteria are further implemented into standards, there will have to be much greater use of bioassays to determine the appropriateness of these criteria.

In some instances, the bioassays will have to be done on the more concentrated contaminant source, that is, the municipal or industrial wastewater effluent. The behavior of the contaminant will have to be simulated for the range of physical and chemical conditions, except for dilution, expected in downstream waters. The purpose of the bioassay would be to determine the 96-h LC_{50} and then, through an appropriate application factor, determine whether the apparently excessive concentrations based on the total bulk chemical content of the effluent are likely to be adverse to aquatic life in the receiving waters. This is going to be extremely difficult to do because of the fact that this requires a good understanding of the environmental chemistry of the contaminant in the water of interest. It is rare that there is this kind of understanding. If the concentration of a contaminant in an effluent, after allowable dilution, exceeds the U.S. EPA criterion, then bioassays, using short life-span organisms such as zooplankton, should be conducted on the effluent, using the receiving waters for dilution, to determine whether or not the contaminants present in these waters are, in fact, adverse to aquatic life. Bioassays utilizing *Daphnia* for fresh water or a similar zooplankton species for marine waters will have to be conducted to evaluate whether the apparently excessive concentrations in natural waters are adverse to aquatic life.

In addition to concern about toxicity, several of the chemicals for which the U.S. EPA has developed water quality criteria are of importance because of their effects on man through the use of aquatic organisms as a source of food. If the concentration of a chemical in the water exceeds the U.S. EPA criterion, where the concern is bioaccumulation-bioconcentration in food organisms, then the reliability of the criterion as a measure of water quality should be determined by collecting representative samples of the organisms at several times during the year. In this way, it can be determined whether, in fact, the excessive concentration in the water, based on chemical analysis, results in an excessive concentration in the aquatic organisms, based on FDA limits for the use of the organisms as a source of food for man. It should be noted that simply finding elevated concentrations of a chemical contaminant in an organism does not necessarily represent an adverse condition. Many organisms will have elevated concentrations of a contaminant if the concentrations of available forms of that contaminant in their environment are increased. However, frequently, these elevated concentrations within the organism rapidly decrease to lower levels when the environmental levels are reduced.

It is also important to emphasize that very little is known today about the significance of bioaccumulation of chemical contaminants as it may affect both the aquatic organisms and their use as food. The FDA has established critical levels of contaminants in food for only a few chemicals. Until it is shown that the accumulation of chemicals, for example, cadmium, is adverse either to the organism or to man through the use of the organism as food—that is, until the FDA establishes a critical level for that contaminant in fish—it will be impossible to judge the significance of its accumulation within fish.

Conclusions and Recommendations

The primary conclusion from this review is that it is not a simple task to determine properly the water quality of a body of water, based on chemical analyses. There are many forms of potentially hazardous chemicals in natural waters which are not adverse to aquatic life or harmful to other beneficial uses of the water. There is a wide variety of mechanisms by which a potentially hazardous situation for aquatic life can be rendered innocuous or of minor significance. As more and more water quality criteria are developed, greater attention will have to be given to the proper use of these criteria in evaluating water quality. The approach that is being routinely used today, that is, making a more or less mechanical match between the criteria values and the results of chemical analyses, will probably not continue, since it can readily result in the expenditure of large amounts of funds for the removal of chemical contaminants which have little or no effect on water quality. Thus far, the July 1976 criteria of the U.S. EPA

have not been implemented into water quality standards to any significant extent in many American states. It is important that the implementation of these criteria into water quality standards be done in such a way as to consider properly the various factors discussed in this paper.

The first step in any program designed to utilize chemical data as a basis for judging water quality is the evaluation of the reliability of the data. Once the data have been judged to be reliable, then comparisons can be made between the chemical concentrations found in a water, the water quality criteria which are applicable to that water, and the exposure conditions that are likely to be encountered. Factors such as the form of the chemical, the rates of transformation from one form to another, the general characteristics of the water, the changes in concentration that may occur with time, and the probability of exposure of aquatic organisms to excessive concentrations for various time periods must be evaluated if proper use is to be made of chemical analyses as a means for judging water quality.

The adoption of the U.S. EPA *Quality Criteria for Water* of 1976 [*1*] will probably greatly stimulate work on identifying the actual chemical species of potentially hazardous contaminants present in various types of natural waters. Once a better understanding of this area is achieved, then the significance of each of these forms to aquatic life and to man will have to be determined in order to utilize water analysis data properly as a basis for judging the water quality of a body of water.

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