FINAL REPORT TO:
U.S. AGENCY FOR INTERNATIONAL DEVELOPMENT
AMMAN, JORDAN

A Water Quality Monitoring Program for Jordan

by

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Texas Tech University
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INTRODUCTION

The future economic development of Jordan will be closely tied to how well this country manages its water resources. As a water-short country with waters of highly variable quality, Jordan, like many other countries in similar situations must, if it is to manage its water quality in the most technically-valid, cost effective manner, establish a water quality monitoring program that will assess current surface and groundwater quality and detect significant changes in these qualities before the uses of the waters are seriously impaired. Presented below is a general water quality monitoring program for Jordan. The adoption of a program that follows this approach should provide Jordan with the data needed to properly manage its water resources.

OVERALL APPROACH

The overall approach that should be followed in any water quality monitoring program is a combination of active and passive monitoring. As defined by Lee and Jones 1983a (see Appendix A), passive monitoring is the collection of data for historical record purposes in which samples are routinely collected and analyzed for parameters that are indicative of water quality. The active component of a water quality monitoring program involves site-specific detailed studies of the analytical reliability and the causes of "excessive" concentrations of a contaminant at a particular location. Water quality is
understood to be related to beneficial uses of water and not necessarily to the concentrations of chemical contaminants which may appear in a tabulation of water quality criteria and standards. For further discussion of the relationship between water quality and water quality standards and criteria, consult Lee and Jones 1982 (see Appendix B). As discussed in the report by Lee and Jones 1983b, there is an urgent need for Jordan to establish more appropriate water quality criteria and standards than exist now. This is a key part of developing a meaningful water quality monitoring program in that it establishes those parameters of water quality which are judged by the Jordanians to be most important in protecting beneficial uses of water of importance to that country. This information is needed to properly activate the active components of a water quality monitoring program.

The water quality monitoring program presented below is a generic program which provides general guidance on the overall approach that should be followed. It is important to emphasize that any water quality monitoring program must be formulated based on an experimental approach in which sampling frequency, location, analytical procedures, data handling and review, etc., are all investigated to be certain that they are the most appropriate for the particular situation being examined. It should never be assumed that just because an analytical procedure worked at one location or that because it is a "Standard Method" that it is applicable to other situations; its reliability must be established at each site. This water quality monitoring program is designed to provide a reliable data base to assist current water quality and detect subtle changes in water quality with time or as a function of management program implementation. Those responsible for carrying out this program must be continuously alert to factors that could influence the ability to achieve these objectives. Those establishing-developing a water quality monitoring program must be thoroughly familiar with data utilization in water quality management.
programs. The monitoring program must be keyed to management needs with both short-term and long-range needs being considered.

Several years ago Lee and Jones published a paper that provides guidance on interpretation of water quality data, Lee and Jones 1979 (see Appendix C). The general approach discussed in this paper should be followed in establishing the water quality monitoring program in Jordan.

It is important to note that the generic program discussed below does not consider the ongoing monitoring programs of the Natural Resources Authority (NRA) as well as other agencies. The approach outlined by Lee and Jones 1983b should be followed in setting up this program in which this guide would serve as the basic framework from which an actual water quality monitoring program would be established in Jordan. As discussed by Lee and Jones 1983b, the first step in setting up a meaningful program is to get all of the parties involved in water quality management and interested in water quality monitoring to form a committee which would, as its first primary objective, discuss the respective programs of each agency or entity active at this time and establish a common pool of data and develop procedures for rapid sharing of data once collected. It is only with this type of approach can a cost-effective water quality monitoring program be developed. The development of water quality monitoring programs without the kind of involvement of the various agencies and entities as presented by Lee and Jones could readily result in large amounts of money being spent in water quality monitoring which would be essentially useless in providing Jordan with the kinds of information needed to properly manage its water quality and therefore, the country's water resources.

SAMPLING LOCATION AND FREQUENCY

Presented below is a discussion of the sampling location and frequency that should be adopted during the initial phases of this monitoring program for the various kinds of waters
and situations pertinent to water quality management in Jordan. It is important to emphasize again that this program is a guide to a generic approach for waters of each type. It does not reflect consideration of the data that has been collected previously by various governmental agencies on particular waterbodies. The approach that should be followed in setting up the sample locations and frequencies should first involve the collection of all previous data collected on a particular waterbody. This data should be screened for reliability with respect to analytical procedures used, appropriateness of sampling and sample handling including preservation techniques, and appropriateness of procedures used for data storage and retrieval. The discussion provided by Lee and Jones 1979 and 1983a should be followed in conducting the data review. It was not possible for Lee and Jones to conduct this type of data review during their visit to Jordan in September 1982 since the data that had been previously collected by various governmental agencies on the waters of Jordan was not in a form that was available for review. As a result, at this time, this report has to be restricted to a generic approach with limited input of information that is needed to develop site-specific, cost-effective, reliable approaches for water quality monitoring at a particular location.

GROUNDWATER

Groundwater is an extremely important part of Jordan's water resources. Groundwaters in Jordan range in quality from those that can be used directly for municipal or agricultural purposes with no treatment to highly saline waters which at this time have apparently little utility. From the information provided, it appears that some of the high quality waters are adjacent to low quality waters where pumping of the wells beyond their "safe" yield results in water quality deterioration. The NRA has an extensive water quality monitoring program.
underway at this time on the country's groundwaters. The details of this program and the data obtained from it were not available to Drs. Lee and Jones and therefore it is not possible to utilize the previously collected data to design the most cost-effective, technically-valid approach for monitoring Jordan's groundwaters. A generic approach is therefore presented in this report. In developing this approach, four different conditions or points of concern are considered. These are producing wells, monitoring wells, springs, and site-installations that could cause groundwater quality deterioration. The general characteristics of a generic water quality monitoring program for each of these areas is presented below.

Aquifer Characterization

The characterization of all major aquifers (potable and nonpotable) within Jordan should be delineated in terms of location-size which would include aerial and vertical extent. It appears, although this was not confirmed by Drs. Lee and Jones, that a program of this type is currently underway by the NRA in cooperation with the US Geological Survey with US AID support. It is Drs. Lee and Jones' understanding that a water quality monitoring component of this program has been or will be developed. The details of this program, however, have not been made available to Drs. Lee and Jones and therefore the adequacy of the current program in properly defining aquifer quality characteristics is unknown. In general, however, as part of any program to define aquifer location, water quality sampling should be conducted from all groundwater hydrology-water table monitoring observation wells.

The first phase of the aquifer quality monitoring program should be one of delineating the location of all wells within the country that could potentially be used to sample the aquifer. In developing this delineation, it is important to determine not only the location of the well, but also the well depth, how the well is cased-casing material, backfill around
the casing, the location of perforations in the casing, and when it was developed. Once this information has been compiled, then those knowledgeable on groundwater hydrology of the region should work with those conducting the water quality monitoring program to determine the adequacy of existing wells for sampling the aquifers of the country. If the existing wells are not adequate for this purpose, then additional wells should be constructed.

The aquifer quality characterization program should be designed to provide a long-term reliable data base which could be used to detect changes in water quality of the aquifer as a whole. The parameters in Group A on Table I should be monitored at these wells. The frequency of monitoring should initially be quarterly for the first two to three years, biannually for the next two to three years, and then annually thereafter. It is possible, that in remote areas where there is little likelihood of groundwater contamination, that the frequency of sampling of the aquifer characterization well can be reduced to once every two to three years. In general, the frequency of monitoring groundwaters should be a function of the variability of the data and the potential for groundwater contamination at a particular location. After about two years of quarterly sampling on an aquifer characterization well, it should be possible to predict the characteristics of the well for the next sampling based on past data. When such predictions can be made with a high degree of reliability, then it is possible to reduce the sampling frequency.

The sampling frequency should also be influenced by the concentration range in which the contaminants are found. For concentrations far below or far above the critical concentrations for various water uses such as domestic water supply or agricultural water supply, relatively infrequent sampling can be used. However, wells that have water with concentrations that are just below or just above the critical concentration require more frequent sampling in order to keep a closer watch on the parameters of concern.
The sampling of the aquifer for characterization purposes can be done at either a monitoring well or production well. If this is done at a monitoring well which is not routinely pumped, then an investigative program must be initiated for each monitoring well to determine how the composition of the well water varies with the degree of pumping. A discussion of this approach is provided in a recently authored paper by Lee and Jones 1983c (Appendix D). If the sampling is at a production well, then an attempt should be made to sample after approximately similar amounts of production have occurred. For domestic wells this is not a problem since their production is more or less constant, unless of course, they are taken out of service for a period of time. The use of agricultural wells can be highly seasonal. The seasonality of the use should be considered in sampling. Since the point of concern is the quality of the water actually delivered, it is usually best to sample wells during periods of active use. It is likely that significantly different chemical compositions will be found in wells that are used intermittently shortly after the start-up of use compared to the composition after prolonged use. This point is discussed further in the paper by Lee and Jones 1983c.

Domestic Water Supply Production Wells

Domestic water supply production wells should be sampled at a greater frequency than necessary to characterize an aquifer. It is possible that localized contamination could occur which would represent a threat to public health. In establishing the frequency of sampling these wells it is usually best to consider the details of construction and the likelihood of contamination. Once information of this type is available, then the sampling frequencies can be established in a meaningful way. Ordinarily in a new program, sampling frequencies should be established at about monthly intervals and then once the composition of the water has been characterized over a several year period, and it is found to be highly
stable coupled with information that would indicate that there is little likelihood of contamination, then the frequency of sampling can be reduced to quarterly for many, if not most of the parameters. It may be possible to reduce this frequency to biannually or even annually under conditions where there is high degree of protection and little likelihood of contamination. This establishment of the reduced frequency, however, must be based on a clear demonstration from the data of the well that a reduced frequency sampling would not result in significant loss of information or increased public health hazard.

Springs

The surfacing of groundwaters results in the formation of a spring which provides the opportunity to assess groundwater quality of the region. This has to be done quite carefully, however, because the composition of springs is frequently significantly influenced by local contamination which generally makes the sampling unacceptable for aquifer characterization. They are, however, frequently important sources of water for local domestic water supplies and, therefore, must be sampled with high frequency from a public health protection point of view. It is suggested that each spring be characterized in terms of its potential for contamination. Easily contaminated springs should be sampled every two weeks until it is shown that a less frequent sampling, such as once a month, is adequate. Monthly sampling is generally appropriate for springs used for water supply purposes. With springs and other wells used for domestic purposes, it may be appropriate to maintain a fairly high frequency of sampling for certain parameters such as fecal coliforms and a much lower frequency sampling for toxic metals and many other parameters. The sampling of a spring for any purpose should always include temperature and specific conductance measurements in order to detect gross changes in the total salt content of the water. If such changes occur, then a higher frequency sampling program should be adopted.
The NRA has published a report on some of their sampling of springs in Jordan (NRA 1979). Review of this report shows that the program maintained by the NRA on sampling of water quality in springs is inadequate compared to what should be done to properly characterize the water quality of Jordanian springs both in terms of frequency of sampling and parameters measured. It is important to note that springs which are used for domestic supply purposes are probably sampled more frequently for their sanitary quality by the Department of Health or other agencies. The exact program followed by the Department of Health and other agencies is not known, however, at this time.

Special Purpose Sampling Near Source of Groundwater Contamination

Potential sources of groundwater contamination are usually fairly easily defined and should be monitored. A tabulation of all such sources in Jordan should be compiled, and specific monitoring programs should be developed for any source that could cause significant contamination of a major aquifer of importance to the country. Included within the tabulation should be such sources as domestic refuse-garbage disposal areas, industrial solid waste disposal areas, areas of intense agriculture such as near Amman and in the Jordan Valley, near industrial sites where large amounts of chemicals are stored or processed such as refineries, oil storage areas, chemical manufacturing operations that use waste disposal lagoons, as well as existing or potential areas where domestic wastewaters are disposed of by land irrigation, areas where mining or mineral beneficiation is taking place, at low-lying areas where urban or industrial surface water drainage tends to accumulate, and areas where sewage or industrial sludge is disposed of on land.

Another potential source of groundwater contamination would be municipal or industrial wastewaters discharge to rivers or streams where there would be infiltration of the
stream waters to the groundwaters. Regions where such discharges occur should be considered potential sources of contaminants for groundwater contamination, and special purpose sampling along the course of the river at each area where there is a significant change in the geology of the river bed should be made.

Another site for monitoring of groundwaters is in the region of proposed impoundments. There are a number of proposed impoundments for Jordan. Monitoring wells should be constructed to monitor the groundwater characteristics in the region of these impoundments since many of them would likely result in groundwater recharge of that region.

It is now proposed to treat Amman wastewaters in several large oxidation ponds, the effluent of which would be used for land irrigation and then return via a stream to the Zarqa River. If this scheme appears to be fairly firm then groundwater monitoring programs should be initiated in the near future in the region of the oxidation ponds and the land irrigation regime. Also, a surface water monitoring program should be initiated on the Zarqa River near where the irrigation return water would enter the river. At each of these areas as well as any others that represent sites of potential groundwater contamination, a detailed hydrologic investigation should be conducted to determine the hydrologic regime that exists in the region, location of the groundwater table and the most probable flow direction from the source to groundwater, estimated rates of flow, etc. Based on this information, a series of monitoring wells should be developed to sample groundwaters in the region.

In placing the monitoring wells, it is important to understand the hydrologic regime of the region. This will likely require a series of pump tests on a preliminary set of wells, the results of which would be used to determine the location of additional wells that could be used to monitor the groundwaters of the region. It is rare that a single well placed in an aquifer near a potentially significant source of contaminants
or groundwater systems will adequately monitor the groundwaters. Normally nests of wells constructed to various depths within the aquifer such as described by Lee and Jones 1983c are needed. If the contaminant source is likely to have a density significantly different from the groundwaters of the region, then wells which specifically sample the surface layers of the aquifer as well as near the bottom of the aquifer, should be constructed and monitored.

In areas in which there is a high probability for groundwater contamination by highly hazardous materials such as where intensive use of pesticides is occurring near certain industrial manufacturing operations using waste disposal lagoons, at hazardous waste disposal sites, municipal garbage-refuse disposal areas, etc., it is highly desirable to establish groundwater monitoring programs which measure contaminant concentrations in the unsaturated zone, i.e., in the water percolating through the area above the water table. Sampling in these areas require the use of tensiometers and cores or other devices in order to obtain appropriate samples of the percolate water. The sampling of the waters in the unsaturated zone is an area of investigation at this time by Drs. Lee and Jones. Should it be desirable to initiate a program in this area, those developing the program should contact Drs. Lee and Jones for their recommendations at the time of program development.

At each monitoring well, the bulk characteristics of the groundwater as well as special characteristics such as those listed in Table I, Group A should be monitored. It is recommended that the monitoring be done at quarterly intervals for two years and then biannually for several more years and then eventually annually. This would presume that after several years it is possible to predict the composition of the waters based on the previous sampling of the wells. Once this can be done with a high degree of reliability, then the frequency of sampling can be reduced. It is also possible that under
special cases the number of parameters analyzed for a particular location could be significantly reduced based on the characteristics of the source.

It is also likely that other parameters would need to be added to the list, especially organics where a particular industrial operation would use large amounts of low molecular weight organics which could be transported to groundwaters. An inventory of all chemical usage at each industrial operation should be prepared. Also, an assessment of any transformation products arising from such chemical usage should be made in order to determine what chemicals should be monitored as a special requirement at a particular location.

Another type of area that deserves special attention as a potential source for groundwater contamination are areas of intense agriculture. Of prime importance to Jordan is the Jordan Valley Authority (JVA) development. While JVA indicated to Drs. Lee and Jones that they plan to develop a water quality monitoring program, it is our impression that at this time such a program is not underway even though intensive agriculture is being carried out in this region. All such development of agriculture should be preceeded by a groundwater quality monitoring program which was established prior to any significant activities in the region. This same situation applies also to industrial developments. In intensive agricultural areas, the parameter list should be expanded to include pesticides, fertilizers, herbicides or other materials used in these areas. Once a particular herbicide or pesticide is used, then continued monitoring of that material should occur for many years.

MUNICIPAL WATER SUPPLY SYSTEMS

Water quality monitoring for Jordan should include specific programs designed to consider changes in water quality within the municipal distribution system. Two major areas of concern should be addressed. One of these is the deterioration
in water quality due to the corrosion, slime growth, or other phenomenon within the distribution system. The other is the contamination of the waters within the distribution system due to the fact that the water supply authorities in Jordan are not able to keep the distribution system under positive pressure at all times. For all municipal systems, a set of samples collected at approximately monthly intervals initially for the first two years and then quarterly intervals thereafter, should be obtained from the household taps at selected locations throughout the system. Usually six to ten sample locations are adequate for this purpose. Such a sampling program would provide the kind of information needed to judge the overall quality of the water delivered to the home. In those systems where at least 40 psi pressure is not maintained on a continuous basis throughout the system, then special purpose sampling should be conducted in order to detect problems of contamination of the distribution system waters due to leakage of domestic wastewaters and industrial wastes into the water supply distribution system from the sewage collection system, cesspools, or infiltration through the surface of the ground.

Since there is a requirement in Jordan of maintaining a residual chlorine in municipal water supply systems, a combination of residual chlorine and fecal coliform analyses should be conducted at approximately weekly intervals, at approximately a dozen or so locations for any municipal water supply distribution system that is not maintained under high-positive pressure at all time. In any system where residual chlorine is not maintained throughout the system and which have high elevated concentrations of fecal coliforms, special provisions should be made to sample these areas more frequently until such time the fecal coliform count can be reduced to about 2 fecal coliforms per hundred milliliters of sample.

Special considerations should be given to the trucked water in which sampling of the source of the water used to fill the trucks as well as the water that is delivered to a
consumer should be conducted to insure that trucking of the water does not result in contamination by chemicals or diseased organisms. Generally sampling at monthly intervals of these waters would be adequate unless they start to show fecal coliform contamination; then high frequency sampling should be undertaken.

SURFACE WATERS

The sampling of surface waters in Jordan is restricted to three kinds of waters: fresh water rivers, the Jordanian impoundment-King Talal Reservoir, and the marine waters of the Gulf of Aqabah. The general approach for assessing water quality for each of these waters is outlined below.

The establishment of water quality monitoring programs for surface waters is significantly different than for groundwaters. Groundwaters have a relatively constant composition. Further, the beneficial uses of such waters are restricted to two fairly well defined uses - domestic water supplies and agricultural water supplies. The critical concentrations of many contaminants that would impair these uses are fairly well known and it is fairly easy to establish whether impaired uses have occurred. Surface waters, on the other hand, in addition to potentially serving as sources of municipal, industrial, and agricultural water supplies have a wide variety of other potentially significant uses that range all the way from fish and aquatic life propagation through the transport and treatment of municipal and industrial wastes. The critical concentrations for affecting the various uses of surface waters are not nearly as well established. Further, there are degrees of impairment of use which have to be considered in formulating an appropriate water quality monitoring program for surface waters. This point is discussed further below as part of developing a water quality monitoring program for the Zarqa River.

Several years ago, as part of some work that was being done on the US-Canadian Great Lakes during the International
Hydrologic Decade, Dr. Lee developed an extensive discussion of approaches that should be used in setting up surface water quality monitoring programs. This discussion is presented in Appendix E of this report. Appendix E presents a general guideline developed by Drs. Lee and Jones that should be followed in establishing any water quality monitoring program. While this guideline is specifically developed for US-Canadian Great Lakes, it is applicable to all kinds of waters. The same questions should be asked in any water quality monitoring program development. Only after each of these questions have been addressed in an appropriate way should the program be initiated other than for preliminary data collection which would be necessary to define the variability of the system.

Rivers

From the information provided to Drs. Lee and Jones, it appears there are two rivers in Jordan which should be routinely monitored. If there are other rivers that exist in that country, the same kind of program as outlined below should be developed for them as well.

The rivers of concern are the Zarqa and the Yarmouk. Drs. Lee and Jones had the opportunity in September to visit the Zarqa River from the King Talal Dam to its origin at the domestic wastewater discharges of the city of Amman. During this visit, which is at one of the driest parts of the year, the river consisted primarily of municipal and industrial wastewaters. It also appears to receive some drainage from springs. The river was essentially an open sewer since poor treatment of the municipal and industrial wastewaters was being achieved at this time. At other times of the year, however, an appreciable dilution of wastewaters occurs due to land runoff. Some of the land runoff, especially from municipal and industrial areas as well as agricultural drainage, could be highly contaminated with a wide variety of potentially
hazardous materials which could impair beneficial uses of the river as well as the King Talal Reservoir.

The sampling of rivers for water quality purposes should be developed based on two general considerations. One of these is the water quality of the river as it may affect beneficial uses of the river, and the other is the load of contaminants the river transports to the reservoir. In the case of beneficial use impairment of the river, the primary concern is that of the concentration of contaminants that may have an adverse impact.

For the impact on the reservoir, the focus of concern is the load, i.e., kg per day, month, or year, that the river transports to the reservoir. For the later types of measurements, it is important to establish a stream gaging system which preferably continuously measures river discharge. Such a station should be located just above the point where the river enters the reservoir but outside of the zone of the influence of the backwater of the reservoir on water elevation within the river. While not visited by Drs. Lee and Jones, they were informed that the NRA or possibly JVA maintain a stream gaging station on the Zarqa River just upstream from the point where the river enters the reservoir. It is not known whether there is a continuous measurement of discharge at this point, however. If not, then a continuously recording stream gage should be established there provided that the gaging system is an appropriate location for such a station where a reliable rating curve can be developed. The US Geological Survey personnel assisting the NRA can readily check out the appropriateness of this location for a stream gage.

It may also be appropriate to establish stream gages at other locations on the river in order to determine the load of contaminants from various sources such as municipal or industrial wastes discharges, tributaries, etc. There may also be removal of contaminants from the area due to groundwater infiltration, volatilization, and agricultural uses. It
is recommended that a gage be established just above the point at which the Amman domestic wastewater treatment plant discharges to the river. During the dry season there is no flow at this point, however, there is appreciable flow at other times and it would be important to determine the amounts of contaminants added to the river from upstream sources during the periods of flow.

Since the river is acting as an extension of the treatment plant, and since the degree to which this is occurring at this time is not known, it would be appropriate to consider establishing another stream gaging system just downstream from where the Amman wastewater treatment plant discharges to the river if there is not a reliable measurement of the amount of this discharge as well as on any of the tributaries that bring an appreciable flow to the river during the wet and dry season. A gage about halfway down the length of the river just beyond the urban-industrial area would be desirable in order to determine the load of contaminants at this point and thereby assess the amount of additional treatment that takes place from this point to the point at which the river enters the reservoir.

A special aspect of sampling of rivers in Jordan that should be incorporated into the water quality monitoring program is the development of a high intensity sampling program at the first major rainfall event following the end of the dry season. The long dry spell during the spring-summer creates a situation in Jordan in which a wide variety of contaminants accumulate within the streets, river beds, and in other areas. With the first heavy rain, a large flux of contaminants occurs in a relatively short period of time. While the sampling of the river where the domestic wastewaters are added can be done on a fairly uniform sampling frequency, such as once a month, the sampling associated with contaminants from dry land runoff must be done according to stream flow at frequent intervals during the first major runoff event.
and periodically during each major runoff event throughout the wet season. Generally, about four samples taken during the first major event where two are taken on the rising hydrograph and two are taken on the descending hydrograph is adequate to characterize contaminant concentrations and loads.

Particular attention should be given in developing the surface water quality monitoring program to Appendix E in which each of the questions on areas of concern, are carefully considered by those organizing the water quality monitoring program. It is extremely important in developing a program for the Zarqa River that the objectives of this program be carefully delineated. It appears from some of the work that has been done in the past, that this has not been done and that somewhat of a "grab bag" approach has been used. Drs. Lee and Jones find themselves in a position of not being able to define the specific water quality monitoring program that should be conducted on the Zarqa River since the previously conducted studies' data has either not been made available to them or has been developed by unreliable analytical procedures. Much of the work that has been done by the RSS has used procedures that are not reliable for measurement of the parameters which they have reported. The NRA program results on the Zarqa River-King Talal Reservoir has not been made available to Drs. Lee and Jones. A report covering these results should be made available within a year according to representatives of the NRA. The measurement of contaminants at each of the proposed gaging stations as well as in the discharges of municipal and industrial sources, should be based on a total contaminant and soluble contaminant analyses in which soluble is operationally defined as that portion that passes through an acid-rinsed 0.45 μm membrane filter. It is important to note that membrane filters of fairly uniform pore size of approximately 0.5 μm pore size should be used. Paper, glass fiber or other filters are not reliable for this purpose.

It is unclear from discussions with various groups as to what, if any, beneficial uses of the Zarqa River are being impaired by it being utilized as an open sewer for municipal and
industrial wastewaters discharged from the Amman-Zarqa region. While not confirmed, Drs. Lee and Jones' discussions with Jordanian representatives that appear to be knowledgeable in the hydrology of the river, it appears that if the wastewaters from Amman were not discharged to the river, that the river would be dry for substantial parts of the year and, therefore, would not support a "balanced" desirable aquatic life population. This situation raises serious questions on the important parameters that should be monitored. There seems to be little point in spending substantial amounts of funds monitoring a wide variety of parameters in the river which are of importance to the maintenance of aquatic life in the river. One of the first activities that needs to be done as part of development of a water quality monitoring program for the Zarqa River, is the development of a committee that would decide what is an appropriate use of the Zarqa River under the current situations that exist in Jordan in which domestic wastewaters from Amman and several other communities constitute the only flow to the river throughout substantial parts of the year. It could be that "The Zarqa River Commission" might decide that they would want to make the river suitable for fish and aquatic life. If so, then the kind of monitoring program that is appropriate for fish and aquatic life should be developed and implemented. If however, its use is that of domestic water supply, then a markedly different water quality monitoring program should be developed.

If on the other hand, the primary beneficial use of the Zarqa River during most of the year is conveyance of partially treated domestic wastewaters to King Talal Reservoir, then the primary consideration for a monitoring program should be that of aesthetic quality and public health arising from body contact by children playing in the water. Previously, the river had been used for river flood plain irrigation. The cholera situation caused the government to terminate such activities. It is possible to reactivate certain kinds of agricultural activities in the flood plains without significantly endangering
public health. A variety of agricultural crops could be grown which would not represent a threat to public or animal health that would consume the crops. A water quality monitoring program specifically directed to this area should be conducted, however, to ensure that there is not some affect on the crop or transport of contaminants from the water through the crop to animals or man.

It is suggested that for planning of the water quality monitoring program for the Zarqa River be directed by the assumption that the river is to be used primarily for fish and aquatic life and domestic water supply. It is important to understand, however, that just because the concentrations of contaminants found in the river exceed those which are suitable for these uses, that this does not represent a significantly detrimental situation for the beneficial uses of the river since it is certain that the river would never be used for domestic water supply. Further appreciable treatment of contaminants present in the wastewaters discharged to the river, occurs by the time it reaches the King Talal Reservoir.

There was some discussion during the meeting with University of Jordan personnel about conducting benthic organism surveys on the Zarqa River. It does not appear that water quality monitoring programs focusing on benthic organisms in the Zarqa River would be highly cost-effective or very meaningful since the aquatic organism populations in the river are going to be highly "disturbed" due to the hydrologic regime even if highly treated wastewaters were discharged to the river.

The assumption that the river is used for domestic water supply purposes and for fish and aquatic life for the purpose of developing a water quality monitoring program would be of value with respect to predicting the impact of the river's discharges on King Talal Reservoir beneficial uses as well as defining the sources of contaminants for the river-reservoir which could have an adverse effect on the reservoir uses. It is suggested that the monitoring program include the parameters
from Table I, Group A plus selected parameters of Group B.
In addition to the chemical parameters listed, it is suggested
that two biological parameters be monitored. One of these
is the occurrence of the fresh water snail, Bulinus. Dr.
Hashwa has proposed, as part of the water quality monitoring
program, to do studies on this snail since it serves as an
intermediate host for schistosomiasis. It is proposed that the
Egyptian workers could transfer schistosomiasis from Egypt
to Jordan and thereby introduce this disease into Jordan.

The other biological parameter that should be monitored
is an assessment of acute lethal toxicity to fish, especially
at the point at which the river discharges to the reservoir.
It is suggested two types of aquatic organism toxicity tests
be used. One of these would be devoted to an 96-hour acute
lethal fish test. The other would be the use of a fresh water
crustacean. The latter will give an indication of subtle
effects of contaminants on aquatic life through impairment of
reproduction.

A sampling program for the Yarmouk River cannot be
specified at this time since no information was made available
to Drs. Lee and Jones on the characteristics of this river.
Mention was made that there is an impoundment proposed for
this river. If there is a possibility of constructing an
impoundment on the river, then a pre-impoundment study should
be conducted in order to estimate the water quality in the
impoundment based on the information developed as part of
the US OECD eutrophication study program, Lee and Jones, 1983d.
The river should be also monitored at a location which would
be just downstream of a proposed dam in order to gather the
kind of pre-impoundment data necessary to determine the impact
of the dam and associated impoundment on water quality in the
river. There was also some discussion about the possibility
of diverting some of the Yarmouk River water for agricultural
development. A water quality monitoring station should be
established upstream of the point of the proposed diversion
in order to characterize the water at this point.
MUNICIPAL AND INDUSTRIAL WASTEWATER DISCHARGES

As part of the development of the national water quality monitoring program, a water quality sampling program for municipal and industrial wastewaters should be developed in which at approximately monthly intervals, samples of the wastewaters should be collected and analyzed for many of the parameters of concern such as in Table I, Groups A and B as well as any particular contaminants that could cause problems that are pertinent to the particular industry. Specific monitoring programs should be developed for each industry on an individual basis. This will require site-specific information on the point of discharge of wastewaters and the industry. Also, of concern, is whether the wastewaters are discharged directly to a receiving water or discharged to sewers which transport them to a central treatment works.

A flow measuring device should be installed on each of the wastewater discharges to determine the total contaminant load from the industry or municipality. The sampling program, in general, should represent a 24-hour composite sample in which a composite is made according to flow. US EPA has considerable experience in developing guidance on how to study the characteristics of various types of industries' wastewaters. Information should be obtained from the US EPA of this type for those industries active in Jordan.

One of the industrial wastes of particular concern to the Zarqa River-King Talal Reservoir is the phosphate mining that occurs in the Zarqa River Valley. One of the questions that needs to be addressed in connection with the phosphate mining is that of the algal availability of the phosphorus in the mining wastewaters. It is likely that the degree of eutrophication of the King Talal Reservoir is controlled by phosphorus input. If this is the case, it is important to know the role of the phosphorus discharged by phosphate mining in providing algal available phosphorus to King Talal Reservoir.

The International Joint Commission review paper developed by Lee, et al. (1980) on the assessment of available phosphorus
should be consulted for information on the approaches for estimating the available phosphorus load from phosphate mining as well as any other sources that discharge phosphorus in large amounts to the river which enter the reservoir.

KING TALAL RESERVOIR

At this time, as far as Drs. Lee and Jones could ascertain, there are only two water bodies which would be characterized as lakes or impoundments within Jordan. One is the Dead Sea and the other is King Talal Reservoir. It is unclear as to whether there is any interest in the water quality characteristics of the Dead Sea. If so, then a site-specific water quality monitoring program should be initiated which is directed toward providing data necessary to characterize those contaminants in the waterbody that are of interest.

While a considerable effort has been devoted to the study of King Talal Reservoir, it appears as a review data made available to Drs. Lee and Jones in their visit to Jordan last September, that there is still very little known about the water quality characteristics of the reservoir. This is the result of several factors. First, the NRA data collected for the reservoir is not available for review. Second, the RSS studies of the past several years have involved the use of analytical procedures which are not reliable for measuring water quality characteristics. Third, one of the key sampling stations just upstream from the dam is located in the wrong place and does not sample the deepest waters of the reservoir.

In general, the approach that should be used as the minimum sampling program for King Talal Reservoir is one similar to that developed by Drs. Lee and Jones as part of the US OECD eutrophication study program. A copy of this monitoring program is included in Appendix F. This program focuses on eutrophication management. Since toxicity to aquatic life and man are of potential importance in King Talal Reservoir, the study program needs to be expanded to include parameters indicative of toxicity from Tables 1, Groups A and B.
It is recommended that at least three sampling stations be established on King Talal Reservoir, one of which would be located about half way between the dam and the point at which the Zarqa River enters. Another would be located just upstream of the dam in the deepest part of the reservoir. A third would be located on the arm of the reservoir which is near the dam. At each station, many of the parameters as appropriate in Table I, Groups A and B, should be monitored at least monthly intervals. This program should, if at all possible be conducted on two-week intervals in which some of the parameters of lesser importance from Table I, Groups A and B are monitored once a month or in some cases, once a quarter. Those parameters which are most indicative of the trophic state of the reservoir as well as the pollutional characteristics of the reservoir water should be monitored more frequently until such time as the concentrations of the parameters at various locations within the reservoir as a function of depth can be readily predicted from the previous monitoring data. The frequency of monitoring could at that time be decreased for these parameters. Significant changes in the hydrologic regime such as wet years, dry years, etc., should result in an increased frequency of monitoring of those parameters that are likely to be responsive to these changes in hydrology. It is important to sample the reservoir water column. The program conducted by the NRA in which only surface samples have been taken is of limited value in characterizing reservoir water quality.

At about quarterly intervals for a several year period and then once a year thereafter, samples of fish that could be used for human food should be taken from the reservoir and analyzed for mercury, cadmium, chlorinated hydrocarbons pesticides, and PCBs to determine the build-up of these materials within the fish tissue. Also, at quarterly intervals for several years, samples of water taken near the dam should be subjected to both acute and chronic toxicity tests discussed above.
The phytoplankton in the water column should be determined at at least monthly intervals with chlorophyll being measured every month, preferably every two weeks. The sampling for the phytoplankton should be done with a water bottle such as a Van Dorn, and not a plankton net.

Since there is possibility that the King Talal Reservoir water will be used for domestic water supply purposes, it is recommended that studies be conducted of potential trihalomethane formation for the reservoir water upon chlorination under water treatment conditions. At approximately monthly intervals for a period of a couple of years, samples of the surface waters of the reservoir should be taken to a laboratory where approximately 1 mg/l of chlorine should be added to the water and the trihalomethane content of the water monitored after a period of about six to ten hours. Standard Methods for Examination of Water and Wastewater provides information on the measurement of trihalomethanes. Additional information on measurement of these chemicals is available from the US EPA, Cincinnati, Ohio.

There were several plans mentioned during Dr. Lee and Jones' visit to Jordan for proposed impoundments on intermittent streams that discharge water to the Dead Sea. At each site where there is a substantial probability that such an impoundment could be constructed, a water quality monitoring program should be established in which samples are collected during periods of discharge and analyzed for the chemical content. The design of the monitoring program must be site-specific with considerable attention given to the expected hydrologic regime at that site.

Since rates of sedimentation of reservoirs is an important characteristic, it should be considered in the design of the reservoir; suspended sediment and bed load of the streams which would be impounded should be measured in order to estimate the useful life of the reservoir should it be constructed. The US Geological Survey should be consulted for current methods of assessment of sediment load.
GULF OF AQABAH

There has been some interest in water quality characteristics and the nearshore waters of the Gulf of Aqabah. This interest appears to be related to phosphate containing dust from loading ships. Information should be developed on municipal and industrial wastewater discharges in that region as well as any airborne contaminants. A site-specific monitoring program of the Jordanian waters of the Gulf of Aqabah should be developed. This program should include sampling of fish and other organisms of the region which could be used for human food in order to be certain that excessive concentrations of pesticides, mercury, or other contaminants are not building up in the food web to cause the organisms to be unsuitable for use as human food.

SAMPLING OF AGRICULTURAL CROPS

In connection with sampling of water quality in agricultural areas, it is also important to establish a monitoring program for the crops produced from water supply sources which have been highly contaminated with various kinds of contaminants that range from human pathogens, heavy metals, pesticide, herbicides, etc. A program of selectively sampling the animals and plants should be conducted. Further, if the crop is used for animal feed, then sampling of the feed stock as well as the meat should be conducted to be certain there is not a potential hazard either to the animals or to man who utilizes the animals as food. The sampling of materials of this type would have to be based on an experimental evaluation of the number of and types of samples that will be needed on a site-specific basis. As a guideline, ten or so representative, somewhat randomly selected samples, should be taken in order to conduct a pilot program from which the variability of the results would be assessed. A detailed monitoring program then could be developed.
The overall approach that should be followed in conducting the analyses is that presented in the 15th Edition of Standard Methods for the Examination of Water and Wastewater published by the American Public Health Association (1981). The specific procedures that should be followed are delineated in Table I.

During the visit to Jordan, it became clear that there was a lack of understanding of fundamental analytical chemistry principles, especially the differences in the reliability of the analytical methods of water analysis in some of the laboratories doing water quality studies in Jordan. It is extremely important that the procedures delineated in Table I be followed unless it can be demonstrated after carefully documented studies that other procedures will provide at least equal accuracy and precision. This will require parallel analyses using both procedures over the period of a year on a particular water in which it is proposed to use the alternative procedure. It is important that the use of the field test kit such as the Hach Kit not be continued. While there are a few analyses in which Hach Kits are reliable, in general, they are not reliable methods for establishing a data base necessary for water quality management.

It is important when setting up a water quality monitoring program of this type to utilize analytical procedures which detect the parameter of concern at least half an order of magnitude below the critical concentration for that parameter, for example, cadmium is a concern of domestic water supplies at 10 μg/l. The analytical methods used should be able to reliably detect cadmium at at least 5 μg/l and preferably 1 μg/l. There are some parameters which are now recognized as having a deleterious effect on man when consumed through his water supply or food at concentrations which are below those which can be readily detected in water with the analytical methods available today. Under these conditions, it is important to emphasize that the most reliable analytical methods available should be used and...
research funds should be made available to improve the sensitivity of the method in order to detect potentially hazardous concentrations with reliability. In reporting data of this type, the concentrations which are less than the detection limit should be reported as less than the detection limit with the specific numeric value indicated. These values should not be reported as zero. In averaging data, the average should be computed with the numbers considered to be zero and the detection limit indicating that the actual values are somewhere between these two extremes.

QUALITY CONTROL PROGRAM

During a visit to Jordan last September, Drs. Jones and Lee found that the various laboratories conducting water analysis in Jordan were not following appropriate laboratory quality control programs. A key part in developing a reliable water quality monitoring program is the quality control program used in the laboratory. General aspects of a laboratory water quality control program are presented in the first section of Standard Methods. All laboratories conducting analyses as part of this program should become familiar with and follow the general procedures outlined in pages 3 to 52 of Standard Methods. Procedures delineated in the US EPA "Handbook for Analytical Quality Control in Water and Wastewater Laboratories" EPA (1979) should be followed in conducting the laboratory quality control program. Based on the experience of the authors and others such as the Environmental Protection Agency-Cincinnati, it appears that as a minimum about 10 percent of the samples should be re-run. Further, about 15 percent of the samples should be spiked with known amounts of a chemical being analyzed. At least once every day, a known reference sample should be substituted into the sample set for processing as an unknown.

SPECIAL ANALYSIS

Selected samples of surface and groundwater should be analyzed for their radioactive components to determine gross

Also, selected samples of surface and groundwater, especially those taken from near industrial areas should be analyzed for the organic compounds and chlorinated hydrocarbons on the US EPA toxic pollutant list for which water quality criteria have been developed as published in the US Federal Register, Volume 45, Number 231, November 28, 1980. Copies of this Federal Register are available on request. The analytical procedures to be used for these chemicals should be those recommended by the US EPA. This agency should be contacted for the latest methods at the time there is interest in conducting these analyses.

GROUNDWATER QUALITY PARAMETERS AND SAMPLE HANDLING

The measurement of parameters in groundwater samples should be based on soluble non-filterable species. If the sample shows any turbidity, i.e., it appears cloudy, then the total contaminant concentration should be measured as well. It is important in handling the groundwater samples to ensure that the pH and redox conditions are maintained essentially as they occur at the time as the waters are removed from the aquifer. Further information on this topic is provided in the review by Lee and Jones 1983c.

Questions about any of the recommended procedures set forth in this monitoring program should be directed to the authors.
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Procedure Section</th>
</tr>
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<tr>
<td>Conductivity</td>
<td>205</td>
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<tr>
<td>Temperature</td>
<td>212</td>
</tr>
<tr>
<td>Turbidity</td>
<td>214A with the Hach 2100A Turbidimeter</td>
</tr>
</tbody>
</table>

**Heavy Metals - General**

- Sodium: 303 A or 325 B
- Potassium: 303 A or 322 B
- Antimony: 303 A
- Cadmium: 303 B or 304
- Chromium: 303 B, 304, 303 A or 312 B
- Cobalt: 303 B or 304
- Copper: 303 B, 304, 303A, 313B or 313C
- Iron: 303 B, 304, 303 A or 315 B
- Lead: 303 B or 304
- Manganese: 303 B, 304, 303 A or 319 B
- Nickel: 303 B, 304 or 321 B
- Silver: 303 B or 304
- Zinc: 303 B, 304 or 328 D
- Mercury: 303 F
- Arsenic: 303 E or 307 B
- Selenium: 303 E or 323 C
- Aluminum: 303 C or 306 B
### Analyses to Be Performed on All Water Samples

<table>
<thead>
<tr>
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<tr>
<td>Barium</td>
<td>303 C and 308</td>
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<tr>
<td>Beryllium</td>
<td>303 C, 309 B, 303 D</td>
</tr>
<tr>
<td>Calcium</td>
<td>303 A or 311 C</td>
</tr>
<tr>
<td>Magnesium</td>
<td>303 A or 318 C</td>
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<tr>
<td>Alkalinity</td>
<td>403</td>
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<tr>
<td>Boron</td>
<td>404 A or 404 B</td>
</tr>
<tr>
<td>Bromide</td>
<td>405</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>406 A, 406 B or 406 C</td>
</tr>
<tr>
<td>Chloride</td>
<td>407 A, 407 B or 407 C</td>
</tr>
<tr>
<td>Fluoride</td>
<td>413 B or 413 A</td>
</tr>
<tr>
<td>Ammonia</td>
<td>417 A &amp; 417 C, 417 D</td>
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<td>Nitrate</td>
<td>418 C or 418 F (Some groundwaters may be analyzed by 418 D)</td>
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<td>Nitrite</td>
<td>419</td>
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<td>Dissolved Oxygen</td>
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<td>pH</td>
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<td>Phosphorus</td>
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<td>303 A, 425 D or 425 E</td>
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<td>Sulfate</td>
<td>426 C or 426 D</td>
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<td>Organic Carbon</td>
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<td>Fecal Coliforms</td>
<td>908 C or 909 C</td>
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<td>Hardness</td>
<td>314 A or 314 B</td>
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<td>Parameter</td>
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<td>Color</td>
<td>204 A or 204 B</td>
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<tr>
<td>Residue</td>
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<td>Salinity</td>
<td>210 A,B, or C</td>
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<tr>
<td>Strontium</td>
<td>303 A or 326 B</td>
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<td>Acidity</td>
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<td>Chlorine (residual)</td>
<td>408 C or 408 D, 408 F</td>
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<tr>
<td>Cyanide</td>
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<tr>
<td>Organic Nitrogen</td>
<td>420 A or 420 B</td>
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<td>Sulfide</td>
<td>427 C or Orion Ion Selective Electrode</td>
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<td>Oil and Grease</td>
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<td>Oxygen Demand (Biochemicals)</td>
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<tr>
<td>Chemical Oxygen Demand</td>
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<td>Pesticides Organic (Chlorine containing)</td>
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<td>Parameter</td>
<td>Procedure Section</td>
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<tr>
<td>Chlorinated Phenoxy Acid Herbicides</td>
<td>509 B</td>
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<tr>
<td>Phenols</td>
<td>510 A &amp; 510 B, or 510 D</td>
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<tr>
<td>Surfactants (Anionic)</td>
<td>512 A</td>
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<tr>
<td>Aquatic Organisms Bio-assays</td>
<td>96-hour Acute Lethal Test &amp; Daphania Toxicity Test. Use latest procedure from American Society for testing materials.</td>
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<td>Phytoplankton</td>
<td>1002 C--2. Membrane Filtration &amp; 1002 F</td>
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<td>1002 G--1. Spectrophotometric</td>
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<td>Fecal Streptococcus</td>
<td>910 B</td>
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</table>
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B. Water Quality Standards and Water Quality
C. Interpretation of Chemical Water Quality Data
D. Guidelines for Sampling Groundwater
E. Great Lake Water Quality Monitoring Programs
F. US OECD Eutrophication Monitoring Program
ACTIVE VERSUS PASSIVE WATER QUALITY MONITORING
PROGRAMS FOR DOMESTIC AND INDUSTRIAL WASTEWATER DISCHARGES

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Fort Collins, CO 80523

INTRODUCTION

One of the keys to developing an appropriate technical information base for evaluation of the performance of particular industrial or domestic wastewater treatment plants and of the environmental impact of the contaminants discharged by these plants on receiving water quality is the water quality monitoring program. Most water quality monitoring programs are what can best be described as passive programs in which data are collected at fixed, rather arbitrary sampling stations at fixed, arbitrary sampling frequencies, and are stored in a file drawer or computer data retrieval system until someone, usually years later, tries to use the data. Their classification as "water quality" monitoring is often inappropriate, as the water quality component is typically negligible or lacking; it would be more
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Colorado State University, Department of Civil Engineering, Environmental Engineering Program. Occasional Paper Number 55, December (1980).
appropriate to label them "water characteristic" or "water contaminant" monitoring programs.

Those who establish "water quality" monitoring programs usually have one of two different points of view or interests. One is that of the regulator or pollution control agency which seeks answers to questions such as, "Is a particular wastewater treatment plant(s) adding excessive amounts of contaminants compared to effluent limitations or causing state water quality standards violations?" The other is that of the discharger or entity responsible for contamination, who is concerned about the impact of these discharges on the beneficial use of the receiving waters. Unfortunately, both of these groups tend to follow passive monitoring programs that often provide little in the way of useful information, compared to what could be gained if an active water quality monitoring program had been designed and conducted. This paper presents a discussion of some of the factors that should be considered in developing cost-effective, technically valid active water quality monitoring programs.

WATER QUALITY

The first step in developing a water quality monitoring program is to make an assessment of those particular aspects of water quality which are of concern at a particular location. Water quality is not, as is commonly assumed,
equivalent to a table of chemical analytical results. As discussed by Lee et al.,\(^1\) water quality must be judged in terms of the beneficial uses of the particular receiving water to man. These uses can include preservation of resident or desired fish and aquatic life, drinking water, agriculture, aesthetic enjoyment such as sitting on the bank and looking at the water, and others. Far too often attempts are made to use the total concentrations of a "laundry list" of chemicals as a measure of water quality. While this is an administratively simple approach, it is, more times than not, technically invalid and wastes public funds. This is in part because chemicals exist in aquatic systems in a wide variety of forms, only some of which can affect water quality, i.e., impair a beneficial use. The concentrations of available forms of the contaminants must remain elevated for a sufficient period of time and over a sufficient areal extent to induce an adverse effect on organisms or characteristics of concern. Further, the induced effect must adversely affect the designated desired beneficial use of the water in order for "water quality" to be impacted. High concentrations of chemicals (especially measured as total concentrations) can generally occur for short periods of time without adversely affecting beneficial uses. The concentrations of certain contaminants in a waterbody can, in many instances, exceed the US EPA Red Book criteria or state water quality standards equivalent to these criteria, by orders of magnitude without a significant impairment of
beneficial uses occurring, provided that the duration of exposure of organisms is sufficiently short. For further discussion of how chemicals affect beneficial uses of water, consult Lee et al.¹

Once the beneficial uses of concern have been defined on a site-specific basis, then a program needs to be developed through which an evaluation can be made of how the discharge from a particular source affects these uses. The results of chemical analyses for selected parameters at fixed locations may provide an indication of where potential water quality problems exist and lay groundwork for additional studies on those areas. However, if the water quality monitoring program design remains passive and is not adjusted to consider on a site-specific basis how the beneficial uses of a particular waterbody are affected by physical, chemical, and biological contaminants and the concentration of available forms - duration of exposure relationships existing there, it is not a technically sound program for water quality management.

ACTIVE WATER QUALITY MONITORING

In order to be cost-effective, water quality monitoring programs should be active, not passive. That is to say, the program should incorporate sampling sites and frequencies and parameters for measurement which have sound technical justification: the program should be sufficiently flexible
to be adjusted on the basis of analytical findings; and there should be a short turn-around time between sample collection and data review by those responsible for administration of water quality at a particular location. Data should never be collected and filed without critical examination by individuals knowledgeable in the area of the impact of chemical contaminants on beneficial uses of water. In general, the turn-around time between sample collection and data review should be no more than two weeks. In this way those responsible for water quality management will have the option of collecting additional samples within essentially the same season, should unusual results be found.

The critical review of the data as they are generated from the laboratory or field measurements should not be limited to ensuring that the numbers have been reliably transposed from the laboratory or field notebooks to master data sheets or the computer data storage system, although this type of data review should be a regular part of all active and passive contaminant-water monitoring programs. In active programs, however, the additional step of assessing the significance of the data relative to threatening or impairing beneficial uses should be made. For example, a typical water quality monitoring program would include measurement of the total copper concentration downstream of the point source discharge containing copper. These data should be examined immediately in a "hazard assessment" format to see if the total concentration of copper exceeds the
state's worst-case standard for copper. If the standard were exceeded, then the person conducting the data review should immediately check with the laboratory to be certain that an error was not made in data manipulation. If no errors were found, then an additional set of samples should be taken to determine whether or not the "excessive" concentration was a spurious value or is a common occurrence. If it appears that the situation could be adverse to the receiving waters, then additional studies of the type briefly described below and in detail by Lee et al, designed to evaluate the real hazard that copper represents to beneficial uses of the water, should be undertaken.

During the past ten years or so, considerable emphasis has been placed on the use of computers to statistically manipulate so-called water quality monitoring data. With few exceptions, efforts of this type are largely mathematical games; the information provided on the actual water quality at the site at which data were collected is typically little more than that which could be gleaned by simply visual inspection of the data. It is generally more advantageous in terms of water quality management to add a water quality component to the contaminant monitoring program than it is to spend large amounts of money for detailed statistical manipulation of data. The same kinds of problems exist with most of the so-called water quality modeling that is being carried out. Unless these models include concentration of available forms - duration of exposure relationships for
organisms that inhabit or could inhabit the area of concern, they are likely not "water quality" models but rather are contaminant concentration or other type of model.

An active water quality monitoring program should be designed following the general procedures outlined by Lee. Rigid, fixed station - fixed period sampling should be reduced and supplemented with special purpose sampling where needed, with frequency dictated by circumstances and findings of more regular monitoring. A significant part of the total funds available should be set aside for special purpose monitoring designed to evaluate the extent of the receiving river, lake, or other waterbody, which has concentrations of contaminants in excess of values which have the potential to be adverse to the designated beneficial uses of the water. When potentially adverse concentrations are found in routine or other monitoring, special purpose sampling should be immediately undertaken to determine the validity and water quality significance of the apparently high contaminant concentrations. If they are representative of the situation, then studies should be conducted to define the concentration of available forms - duration - distance relationships that exist in the particular waterbody receiving the source of contaminant. This type of information provides an indication of the area, and to some extent the magnitude of the potential adverse effect on water quality. As indicated above, however, it is not a measure of adverse impacts.
Part of the funds available for water quality monitoring should be devoted to toxicity testing since chemical analyses per se generally do not provide reliable indications of water quality impairment. Acute toxicity tests with fish are relatively simple and relatively inexpensive; if properly conducted, they can provide large amounts of useful information about contaminant impact per dollar spent on contaminant control. Toxicity tests with fish or certain other aquatic organisms, such as Daphnia, provide an assessment of both synergistic and antagonistic effects of chemicals and of other factors that influence the toxicity of chemical contaminants. Most importantly, they provide a check on the adequacy of the chemical testing program. Studies of this type can also readily indicate if there is some component which has not been measured which is highly toxic to aquatic life in the receiving waters. While many of these toxicity tests are short-term - acute, it is possible to obtain a considerable amount of useful information on chronic toxicity through the use of Daphnia testing. Since the number of contaminants that will have to be measured in wastewaters will increase significantly in the near future because of the new "toxic chemical" criteria being developed by the US EPA, much greater use is going to be made of aquatic organism toxicity testing as integrators of the total effect of all of the contaminants in a particular water or source. Such testing will, in most cases, prove to be much less expensive and often more reliable than the measurement of the concen-
trations of tens to hundreds of chemical contaminants in a particular waterbody by chemical means.

In 1981 the General Accounting Office released a two volume report to Congress concerned with its analysis of the US EPA and USGS water quality monitoring programs. The GAO report concludes that the current US EPA and USGS fixed station - fixed interval sampling networks are not very effective for assessing water quality. It recommends that the US EPA and the USGS national water quality monitoring networks be discontinued and that a shift in the program be made to special studies of water quality which would be similar to those recommended in this paper. While the authors of this paper do not agree with the GAO with respect to the complete termination of the US EPA and USGS monitoring programs, they are highly in support of the concept that the fixed station - fixed interval approach is not the most valid for assessing water quality in the nation's waters.

According to the GAO report, the agencies' comments on the GAO report indicated that statistical analysis will overcome the complexities of water quality and that valid assessments of the nation's rivers can be made from infrequent (generally monthly) samples of water taken at less than 2,000 locations around the country. The authors wish to take strong exception to this approach; statistical analysis cannot salvage the deficiencies in the USGS and US EPA water quality networks. As discussed in this paper, these deficiencies are inherent in the way the program is set up and operated.
and they will not be eliminated until there is a complete revamping of the program so that it focuses on water quality rather than playing mathematical games with the physical, chemical, and biological characteristics of the water.

The increasing emphasis being placed on land disposal of hazardous wastes requires that greater attention be placed on sampling groundwater. Lee and Jones\(^5\) have prepared a guide to groundwater sampling that should be consulted for further information in this topic area.

**SUMMARY**

The hazard assessment approach, such as that outlined by Lee et al.,\(^2\) should be used as a guide for the development of a water quality monitoring program, as well as in the interpretation of the results of the program. Such a hazard assessment approach allows the physical, chemical, and biological characteristics of the water to be considered in light of their potential impact on beneficial uses of the water by man. As discussed by Lee and Jones,\(^6\) however, the first step in interpreting any water quality data is to review the reliability of the data. The procedures described by Lee and Jones\(^6\) are suggested for use as a guide for this purpose.

**ACKNOWLEDGMENTS**

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Public Law 92-500 has set as a goal—interim to attainment of zero pollutant discharge—the attainment wherever possible of what are generally referred to as fishable, swimmable waters by 1983. To carry out the purpose of this act, water quality standards shall be effected by the states. These standards—the designated uses of the waters and the water quality criteria for such waters based upon these uses—must meet the approval of the U.S. Environmental Protection Agency (EPA) administrator. Public Law 92-500 further mandates that EPA develop water quality standards that accurately reflect the latest scientific knowledge on the effects of pollutants on water. EPA issued its “Quality Criteria for Water” (Red Book) in July 1976 to meet this obligation. If the states fail to provide standards that the administrator feels are consistent with the applicable requirements of this act, EPA must publish proposed standards for that state. EPA’s technical resource for proposing standards is the set of Red Book criteria. Indeed, according to EPA policy, standards can exceed EPA criteria only if the state “provides adequate technical justification for the deviation.”

The EPA July 1976 Red Book criteria are in most cases single numerical concentrations that were developed based on the results of chronic, lifetime bioassays or extrapolation equivalent of sensitive organisms exposed to contaminants in 100% available forms. They and the additional EPA criteria currently out for review therefore are “worst-case” criteria. Increasingly, there are individuals and groups who question the appropriateness of automatically, somewhat arbitrarily, setting water quality standards at concentration levels equal to or less than these worst-case criteria. The zero pollutant discharge goal of PL 92-500 and EPA’s approach for developing state water quality standards based on worst-case criteria was initiated in the “E-day” era of the early 1970s when the environmental conservation movement was at its peak. At that time there was a widespread belief, which continues to some extent today, that “contaminant” and “pollutant” were synonymous and that, if any contaminant entered a water body, degradation of water quality would result. Little regard was given to economic or other social impacts or consequences of fulfilling the “zero contaminant” goal. Although it seemed then that the American public would support and pay for the ultimate in contaminant control to achieve this goal, irrespective of the effect of contaminants on water quality, the growing realization that a contaminant is not necessarily a pollutant, combined with the recent energy crisis and inflation, have led many to question the practicality and desirability of achieving zero contaminant discharge or of treating wastes to meet worst-case exposure criteria-standards.

This ultraconservative approach, it should be noted, has still not been widely implemented within the U.S. The slow rate at which EPA promulgated the water quality criteria (they were due in October 1973 but not published until July 1976) has meant that, in general, states are only now beginning to adopt water quality standards based on these criteria. There have been few instances in which contaminant loads to water bodies have been adjusted based on achieving contaminant levels in the receiving waters at or below these criteria-standards levels. It is beginning to be realized that the control of contaminants from point as well as diffuse sources to meet water quality standards numerically equal to Red Book criteria will

- Require a massive expenditure of public funds, either through taxation or increased prices of goods;
- Aggravate the already short energy supply; and
- Contribute to the inflationary spiral.

As a result, many state pollution control agencies are encountering significant public opposition to the use of worst-case criteria as numeric values for state water quality standards. Further, use of this approach is also being met with increasing opposition from the technical water quality management community because it is well known that contaminants exist in aquatic systems in a variety of forms, only some of which are available to affect water quality/aquatic organisms. The response of aquatic organisms to available forms of contaminants

To achieve desirable water quality, it is not always necessary to make the “worst-case” assumptions.

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![Diagram of Concentration of Available Forms of Contaminant vs. Duration of Exposure](image)

Figure 1—Generalized concentrations of available forms/duration of exposure/"no impact" relationships.

may depend on the duration of exposure of the organism.

Figure 1 illustrates general relationships among organism response, the contaminant concentration, and duration of exposure. It shows that organisms generally can tolerate, with no ill effects, concentrations of available forms of contaminants above chronic safe levels as long as the exposure time is sufficiently short. These factors are not taken into account in EPA's Red Book criteria. Consequently, the more-or-less mechanical adoption of Red Book water quality criteria numeric values as state water quality standards will sometimes result in large-scale expenditure of funds in the name of water pollution control with little or no improvement in water quality as measured by the water's swimmable-fishable characteristics.

The growing opposition to the EPA's worst-case approach is exemplified by a number of recent events. One of the most significant is the statement presented in 1979 by the president's Council on Wage and Price Stability criticizing EPA's position with respect to the state of Ohio's water quality standards. It was recommended that EPA modify its Red Book policy or the Red Book itself to provide criteria in the form of a range of values corresponding to different levels of protection within the waterbody use level. This modification would permit states to consider localized conditions and the expected costs and benefits in choosing specific criteria for a given use level. As indicated by the president's council, issues similar to Ohio's also have arisen recently in connection with the review of water quality standards developed by Indiana, Kentucky, North Carolina, Pennsylvania, and Texas.

Another criticism of the approach taken by EPA and some states for setting water quality standards is exemplified by the actions of the city of Denver, Colo. Denver has asked the public, through a one-page advertisement-questionnaire in a Denver newspaper, what it wished to achieve in the way of water quality in the South Platte River downstream of the major wastewater discharges from the city, in light of the cost of achieving various degrees of contaminant control. Also in Colorado, the cities of Fort Collins, Windsor, and Greeley, and Kodak of Colorado have jointly filed suit against the State Water Quality Control Commission for the purpose of establishing more technically valid and appropriate water quality standards for the waters receiving their wastewater discharges. This group of municipalities and industry was prompted to this action because they felt that the State Water Quality Commission and EPA did not properly consider the ambient conditions of the receiving waters in developing their stream classifications and associated water quality standards. For example, because of irrigation diversions, the only water in the Poudre River below the Fort Collins wastewater discharge is domestic wastewater. When the city discharges to an irrigation ditch instead of to the river, as is frequently done, the river is at times essentially dry. It is doubtful that any type of sport fishery can be established under these conditions. To impose Red Book criteria as a basis for establishing waste load allocations under these conditions is technically invalid and inappropriate, and could easily result in expenditures by Fort Collins and other communities of large amounts of money in the name of water pollution control, with no associated improvement in fisheries, even though the communities achieve the Red Book criteria levels for ammonia and chlorine (which presently are the contaminants of greatest concern) in the river when the wastewater discharges are made to the river.

Congress is also becoming increasingly critical of EPA’s approach toward requiring domestic wastewater treatment beyond normal secondary treatment. The Government Accounting Office (GAO) critique of EPA’s approach for advanced waste treatment has caused Congress to request that EPA conduct a critical review of the potential water quality benefits of constructing treatment plants categorized as advanced secondary treatment or advanced waste treatment and costing in excess of $3 million.

Part of the mounting resistance against EPA's approach is the completely arbitrary use of Red Book criteria for certain situations. One blatant example of inappropriate use of these criteria is in EPA regulations governing ocean dumping of dredged sediments. This subject is discussed in a subsequent portion.

WHAT IS WATER QUALITY?

The first step in developing a plan for pollution control is to define the desired characteristics of water quality. According to PL 92-500, these are "chemical, physical, and biological integrity," and, intermittently, "the
protection and propagation of fish, shellfish, and wild-
life" and provision for "recreation in and on the water"
(fishable, swimmable), wherever attainable. Because of
the close tie made between these goals and water quality
standards and criteria, water quality has unfortunately
and inappropriately come to be defined in some states
by the comparison of chemical concentrations in a water
sample to equivalent Red Book water quality criteria
or standards. As alluded to in the law (which requires
inclusion of the designated uses of the waters as part
of water quality standards), and as classically defined,
"water quality" should be tied directly to the beneficial
uses of a particular water body by man. Beneficial uses
include domestic, industrial, and agricultural water sup­plies, sport and commercial fishing, recreation, and aes­thetic quality as perceived by someone sitting on the
bank or boating on the water.

Until substantially larger amounts of money are
available for research and pollution control, and until
techniques are available to judge much more subtle
biological effects, man and his use of the water should
be the focal point of all water quality consideration.
During the late 1960s and early 1970s, the concept of
aquatic "ecosystem quality" evolved; it is sometimes
advocated that the focal point of pollution control pro­grams should be to control contaminant input to the
point that there is no effect on the numbers, types, and
functions of the various aquatic organisms that live in
a particular water body. Although this concept is in
keeping with zero pollutant discharge, current scientific
capability to detect many such changes is limited and
costly. Also it is well known that the numbers and types
of organisms in an aquatic system may be altered sig­nificantly—in some cases to the point of extinction
of a species—with little or no impact on the functioning
of the overall ecosystem. It is rare, even in situations
not under the influence of contaminants, that the num­bers and types of organisms are constant. Normal cli­matic changes may have a significant impact on eco­systems and specific species within them. The public
does not presently seem to be willing to spend large
amounts of money for water pollution control unless
readily perceptible improvements in water quality will
result. It is important to note that the term "water qual­ity" is being used here in its broadest sense (which can
include the numbers and types of organisms). It is
doubtful that large amounts of public funds are going
to become available to change the number of benthic
worms in a particular aquatic system sediment; for ex­ample, unless there is a reasonably clear relationship
between one type of worm and another in affecting the
water quality components that man would perceive,
such as the numbers and types of fish present in the
water body. It is not now, nor will it likely be possible
in the foreseeable future, to relate subtle changes in
aquatic organism content, especially the lower forms,
to the water quality components of the system that are
of greatest importance to the general public. Fre­quently, the public wants to know number of and whole­somefulness of fish that can be obtained from a particular
water body.

The first step that must be taken to improve water
quality in a particular water body is to define the prob­lem; that is, how are the beneficial uses to man of a
particular water being impaired, and what is the cause
of this abuse? These decisions generally must be made
on a local level and require case-by-case evaluation.
The relationship between beneficial use and acceptable con­taminant load is also site specific; each water body has
its own assimilative capacity. Further, although the
discharge of a contaminant to two different water bodies
may result in the same total concentration in the waters,
the impacts of the load could be considerably different
because the forms of the contaminant in the waters may
be different. Therefore, designing contaminant load al­locations based on meeting a specific worst-case stan­dard-criterion total concentration in the water is inap­propriate. Highest priority for funding water pollution
control should be given initially to those programs that
focus on the most significant impairment of the ben­eficial uses by man.

It is now well recognized that unlimited amounts
of money are not available to devote to water pollution
control. In the 1970s, money spent was usually for the
control of obvious, gross water-quality degradation. As
these situations are abated, funds spent for water qual­ity improvement have been directed toward eliminating
more subtle adverse effects. The cost of controlling these
effects generally will be much greater because of the
low concentrations that must be reached. Likewise, the
benefits derived will be more difficult to discern. There
will have to be, therefore, a much more selective allo­cation of the financial resources available to ensure that
the greatest amount of improvement in water quality
results from the money spent in a particular control
program. As the more perceivable water quality prob­lems or those of most concern or most readily remedied
are eliminated, additional funds should be used for con­trol programs directed toward less readily identifiable
problems. The broad brush, ultraconservative approach
for contaminant control is inappropriate and must give
way to a more carefully developed assessment of what
the real water quality problems are in a particular water
body, definition of the sources of contaminants that
cause these problems, development of a contaminant-
load/water-quality response relationship for a par­ticular water body, and societal decisions regarding the
amounts of money and other resources that should be
spent locally to control the contaminant inputs to the
degree necessary to achieve the desired water quality.
The adoption of this approach will require a markedly
different administrative framework than has existed
thus far in the water quality control field. One reason states have adopted single numeric value water quality standards similar to those of EPA (July 1976) is that these standards are relatively simple to administer. EPA and some state pollution control agencies have opted for this administratively simple approach. However, when fully implemented into contaminant load allocations in the 1980s, the simplicity of the administrative approach will be paid for many times over by unnecessary contaminant control programs that will result in the control of contaminants not affecting water quality in a particular aquatic system.

In general, the first priority for pollution control programs must be toward establishing fishable water to provide at least a moderate quantity of desirable fish that are wholesome and nondamaging to man and animals that use the fish as food. If a water body will support at least a moderate game fish population, then the water usually will be suitable for domestic water supply purposes (normally the highest priority given to a particular water use). There are exceptions to this relationship, but these must be considered on a case-by-case basis.

In the opinion of the authors, after it is possible to establish at least moderate quality fisheries for a particular water body where the habitat is suitable to support the number and types of fish desired, consideration may be given to optimizing the fisheries through the additional control of contaminant input. It should be emphasized, however, that it may not always be in the best interest of the public to try to make all reaches of all water bodies suitable for at least moderate fisheries. The public may feel it is in its best interest to allow certain reaches of a particular stream to have contaminant concentrations outside of the classical mixing zones for point-source discharges to rivers or lakes higher than normally associated uninhibited fish reproduction. An example of this situation would be associated with the use of chlorine for disinfection in municipal wastewaters. Although chlorination is practiced to protect public health, it is being recognized that chlorine in levels present in chlorinated domestic wastewater treatment plant effluent is highly toxic to fish and other aquatic organisms. Granted, chlorine does tend to dissipate rapidly in aquatic systems; this dissipation rate is sufficiently slow, however, that chlorine will in many cases be present outside of the mixing zone typically allowed for municipal wastewater discharges. This means that if a pollution control agency utilizes appropriate analytical techniques, it can detect chlorine outside of the mixing zone in levels in excess of the Red Book criterion. Therefore, if the water quality standard adopted by the state is numerically equal to this criterion, the municipality would be in violation of this standard and would have to reduce the chlorine content of its effluent.

The authors and their associates are currently conducting a study of the persistence and impact of chlorine in the Poudre River downstream of the point of discharge of the domestic wastewaters from the city of Fort Collins, Colo. Fort Collins could be forced to spend over $100,000 for dechlorination equipment and several tens of thousands of dollars per year for dechlorination chemicals, to reduce its chlorine discharge to meet the Red Book criteria. Other nearby cities (such as Loveland, Colo.) have been forced to adopt such procedures, but few studies of the actual persistence and effect of chlorine in the receiving waters have been conducted. The authors' studies have shown that the concentration of chlorine from the Fort Collins plant exceeds the Red Book criterion by several μg/l for about 90 m downstream of the discharge. Caged fish (fathead minnows) placed about 100 m downstream of the discharge remained alive throughout their 1-week exposure to effluent chlorine, as well as any other contaminants present in the effluent. Survival was shorter at locations nearer the outfall, but it is clear that fish can readily pass through the region and spend several days in the area without any readily discernible adverse impacts.

Chlorination could also have an adverse effect on fish food organisms. The quantity of fish food present in the water downstream of the point of discharge of chlorinated effluent may be somewhat less than if no chlorine were added to the river. The difficulties in quantifying sublethal effects on fish, such as might be associated with a diminished food supply, are extreme, however; and it is doubtful in this instance that any change in the fishery would be perceptible. The nature of the reach of the Poudre River affected by the wastewater discharge is such that it is unlikely that a viable sport fishery could be developed without much more substantial management than simply decreasing the chlorine concentration in the effluent, as discussed earlier.

Further, it should be noted that if there is any public health benefit associated with the chlorination of the wastewaters (and there are those who question this assumption for many situations), then extending the contact time would enhance this benefit. In other words, the dechlorination step would tend to increase the public health risk of contracting a variety of enteric diseases from contact with the Poudre River water downstream of the input of the wastewater treatment plant effluent.

Another example of a situation in which a water quality criterion is exceeded and yet a desirable fishery exists is provided by Lake Mendota, Wis., recognized as one of the better warm-water fisheries of the area. Extensive fishing pressure is made of this lake; yet routinely throughout the summer months, the photosynthetic activity of the water body is such that the pH is raised above the Red Book criterion. It is possible that otherwise there might be a better fishery, although this possibility is not at all clear because the only way to
reduce the pH to acceptable levels is to reduce the nutrient inputs that could, in turn, reduce the fish yield. Lee and Jones have discussed the relationship between phosphorus loads and fish yields in water bodies, and have shown a strong correlation between the two. The magnitude of the diel pH fluctuation would therefore also be correlated to phosphorus loads to Lake Mendota. It is certainly inappropriate to apply the Red Book pH criterion to this water body for purposes of improving the fisheries. In fact, the application of this criterion may be detrimental to the fisheries of the lake. It is important to note that Lake Mendota's situation is typical of that encountered in many water bodies considered to have a good sports fishery.

Many water quality control specialists can readily cite numerous examples of waters that have good sports fisheries, yet have concentrations of one or more contaminants that exceed Red Book criteria levels. Although these may not represent the optimum fisheries possible, there are many cases today where, owing to energy and financial constraints, achieving optimum fisheries or other beneficial uses may not be socially desirable. As noted above, this is causing some federal governmental agencies; state and local pollution control agencies; as well as municipalities, industry, and agricultural interests vigorously to oppose the direct use of the worst-case water quality criteria values as water quality standards. Although achieving the optimum fishable waters should still be the ultimate goal, it should not necessarily be the immediate goal.

In summary, water quality should be judged based on the impacts of contaminants on beneficial uses of the water by man; it should not be assessed by the total concentrations of contaminants in a water sample. Because the concentration of a contaminant in a water sample exceeds worst-case water quality criteria like those in the EPA Red Book does not necessarily mean that water quality deterioration is occurring or that the water quality is unacceptable. Water quality control programs should be directed first toward improving gross water quality deterioration that is readily discernible by the public. Only after these problems have been eliminated in a particular region should control efforts and funding be directed toward the more subtle effects of contaminants such as impairment of reproduction, changes in fish behavior, and "ecosystem quality" impacts. These impacts should be controlled to the degree desired by the users of the water and should be in accord with funds made available to do so.

Because there may be very little relationship between water quality and exceeding water quality standards numerically equal to Red Book criteria, it is reasonable to ask how pollution control agencies and municipalities should proceed to achieve the goals of PL 92-500 for swimmable-fishable waters. The financial and resource constraints that exist today will most certainly become more severe in the future. Rather than arbitrarily assuming worst-case conditions exist (as when Red Book criteria values are used to judge water quality), it should be possible for governmental agencies, industry, and others responsible for the source of contaminants to determine the potential zones and magnitude of impact of a particular contaminant or combination of contaminants on given aspects of water quality. Basically, what is needed is an assessment of the contaminant load/water quality response relationships that could inform the public of the water quality benefits that will be achieved as the result of providing certain degrees of contaminant control for certain amounts of their money. Such an assessment procedure, an "environmental hazard assessment approach," is being developed through the efforts of the authors.

HAZARD ASSESSMENT APPROACH

As discussed by Cairns et al. and Lee et al., an environmental hazard assessment for an aquatic system utilizes the combination of aquatic toxicity and environmental chemistry-fate information to determine:

- The forms and amounts of contaminants present in a particular water body that can affect water quality,
- The zone of potential impact for both acute and chronic toxicity, and
- The actual toxicity or other effects that occur in the region.

This hazard assessment is a tiered approach that enables the user to determine, at each level, the need for continued assessment to refine the estimate of the degree of hazard and the acceptability of the hazard that exists for a particular contaminant in a particular system. In some systems it is possible, through relatively simple calculations and without any field work, to determine that there is no hazard or that there may be a very substantial hazard associated with the discharge of a particular chemical. Under these conditions, there is little or no need to proceed with further work to define the hazard more precisely. It is in the in-between situations, where the expected environmental concentrations of available forms are near the critical concentrations that cause an adverse effect on water quality, that there is often need for further work beyond initial screening. Considerable emphasis is placed on the use of bioassays of selected reference organisms that can be related to the potential impact on organisms in the region of interest.

This increased use of bioassays will eliminate the need to analyze water samples for the hundred thousands of potentially significant contaminants that could be present in the effluents of chemical manufacturing plants, other industries, urban stormwater drainage,
and municipal wastewater treatment plants. Actually, probably the greatest use of bioassays will be to determine what part of the total concentration of many contaminants is available to affect water quality. As with chemical analyses, many difficulties are encountered in properly interpreting bioassay data with respect to their water quality implications. To provide guidance on the approaches that should be used for interpretation and appropriate application of bioassay results in water pollution control programs, the Water Pollution Control Federation “Standard Methods”10 Bioassay Section Committee has organized a new subcommittee. Further information on the activities of this subcommittee may be obtained from the authors. It is anticipated that a hazard assessment approach of the type described by Cairns et al.4 and Lee et al.12 will be used as a basis for this subcommittee’s activities.

Table 1 briefly summarizes the testing that should be done in a tiered hazard assessment for interpretation of effluent or stream bioassays, or chemical analysis of a contaminant input source or aquatic system. Further details on each component within this approach are discussed by Lee et al.8 (a copy of the discussion is available from the authors).

The approach that has been used over the years to develop control programs for gross pollution of waters has been based on the measurement of the total contaminant content. This approach is completely unsatisfactory as a means of assessing potential environmental-degradation/water-quality-impairment when the subtle effects of contaminants are the focal point (chronic toxicity, for example). Under such conditions, it is absolutely essential that available (in addition to total) forms of contaminants be measured. The total content of contaminants is useful as an indicator of potential problems; however, it should never be used as an indicator of real problems or as a basis for infliction of contaminant load allocations on either point or diffuse sources, or both. This is especially true, for example, for materials associated with deposited or suspended sediments. The work of Lee et al.11 and Jones and Lee12 has clearly demonstrated that there is no relationship between the total content of contaminants associated with dredged sediments and their impact on water quality when dumped in open water. Further, these works and others have shown that the total concentrations of contaminants in deposited sediments cannot be used to judge in any way the potential impact that those sediments will have on organisms contained within the sediments.

A prime example of the need for a hazard assessment approach for developing control programs for chemical contaminants in aquatic systems is provided by the regulations governing ocean dumping of dredged sediment, Public Law 92-532, EPA.13 and EPA and the Corps of Engineers14 specify that the contaminant concentrations at the edge of a mixing zone of a dredged sediment dump site are to be assessed for their implications for water quality by comparison with Red Book criteria. As discussed by Jones and Lee,12 because of the intermittent nature of ocean dumping operations and the characteristics of ocean water dumping procedures, it is extremely unlikely that organisms in the water column at a dump site can sustain a chronic exposure sufficient to justify the use of the Red Book criterion for a particular contaminant. Further, as discussed above, dredged sediment-associated contaminants are largely in unavailable forms. Red Book criteria should not be used to judge the potential environmental impact of dredged sediment disposal; yet EPA and some states are using these values for this purpose. This situation is resulting in a significant increase in the cost of maintenance of waterway navigability (because alternate, more expensive disposal techniques must be used) with little or no improvement in water quality. In some instances, alternate disposal techniques present a significant increased potential for deteriorated water quality. Instead of dumping the sediments in the open waters where they can be readily dispersed below concentrations that can be harmful to aquatic life, these techniques cause the release of contaminants to the nearshore waters where there is limited mixing and where sensitive life forms of aquatic organisms are present.11,12

In any environmental hazard assessment, the levels of protection must be established with public participation. It is the public, through taxes and the price of goods, that pays for water quality improvement. It is therefore imperative that water quality control programs focus on benefits of public concern. Failure to do so will erode the already limited public faith in the ability of elected officials and governmental agency personnel to improve water quality with available funds.
CONCLUSIONS

Some states are proposing water quality standards numerically equal to EPA July 1976 Red Book water quality criteria. This has been the administratively simple approach for the states to meet their obligations according to PL 92-500 and EPA policy, the latter being that unless the state provides adequate justification, its standards can be no less stringent than the Red Book criteria. However, the Red Book criteria are typically single values that indicate the level of available forms of contaminant to which an aquatic organism may be exposed for chronic lifetime durations without being harmed. Water quality standards and contaminant load allocations should be based on the preservation of the beneficial uses of the water body in question to the extent that the users believe is appropriate based on financial, energy, and other pertinent constraints. To maintain or restore desirable water quality, it is not always necessary to make the worst-case assumptions associated with the Red Book criteria. An environmental hazard assessment approach may be followed to assess the hazard to water quality associated with a given contaminant source. The decision about what constitutes an acceptable environmental risk is a societal one.

SUPPLEMENTAL DISCUSSION

Subsequent to the completion of this paper in 1979, EPA in 1980 released its criteria for 64 of the 65 contaminants named in the consent decree. Although the discussion presented above is applicable to these criteria as well, EPA has also made two important policy changes that may significantly impact the implementation of all of its criteria into state water quality standards.

First, EPA has dropped its policy of “presumptive applicability” of its criteria. Prior to the November 1980 legislation, as discussed in this paper, EPA policy required that if a state adopted a numeric standard for a contaminant, the standard must be at least as stringent as the EPA criterion; that is, the policy presumed the criteria were applicable to essentially all waters. Although PL 92-500 nominally gave states the opportunity to adopt standards less stringent than those of EPA after providing acceptable justification, actual EPA policy was to hold the states to adopting its criteria. Because many state pollution control agencies did not feel that this approach was appropriate, they chose not to adopt numeric standards for many of the parameters for which EPA had developed criteria.

The second major change made by EPA in standards development policy is the requirement that states adopt standards for all parameters for which EPA has criteria. This requirement will have a significant impact on some states’ water quality standards because few states adopted standards for all EPA criteria. Even though the states are now free to develop site-specific standards, there are many, including the authors, who question the wisdom of this requirement, especially as it relates to many of the exotic contaminants that were cited in the Consent Decree “List of 65.” This list of contaminants did not receive proper technical review. Many of the parameters may belong on a list of contaminants of potential concern; they do not, however, belong on a list of parameters for which water quality criteria must be developed. This is especially true in light of EPA’s decision to require that water quality standards be developed for all parameters having EPA criteria. The development of water quality standards for all of the contaminants in the EPA July 1976 Red Book and on the “List of 65” would require a substantial effort on the part of the states, an effort that is certainly not justified for many of the contaminants on the EPA toxic chemical lists.

EPA should, in cooperation with the states, develop a proposed list of contaminants for which standards must be developed. The selection of contaminants for inclusion on this list should be based on factors like potential toxicity and general occurrence in the nation’s waters. There is no justification for developing a state water quality standard for a contaminant that was put on the “List of 65” because someone thought it might be important but for which subsequent studies have not confirmed the potential importance of the contaminant. The inclusion of a contaminant on such a list should be done very carefully because a massive expenditure of taxpayers’ funds will be required for analyses of point-source discharges and natural waters, as well as for site-specific studies. A much more effective approach should be found for selecting contaminants that deserve the expenditure of public funds for the development of national water quality criteria and state water quality standards.

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REFERENCES

G. F. Lee and R. A. Jones

Interpretation of Chemical Water Quality Data


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], 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 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 [11] (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 elasic 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 LC₅₀ 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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GREAT LAKES WATER QUALITY STUDY AND
MONITORING STRATEGY FOR HAZARDOUS CHEMICALS

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INTRODUCTION

It is generally agreed that water quality in some parts of the Great Lakes has deteriorated significantly. However, when an attempt is made to analyze the data base in support of this statement, it is found that there have been very few high quality data generated in support of this conclusion. In the past, there were few, if any, studies conducted which adequately and properly defined many parameters of water quality in the Great Lakes. Therefore, based on current analysis of various water quality parameters, it is difficult to definitively determine whether or not the water quality of the lakes has changed.

There have been numerous studies on water quality in the Great Lakes. In most cases, the individual or agency responsible for the studies would list as an objective the evaluation of current water quality in some parts of the Great Lakes.

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Great Lakes system. However, examination of the results of these studies shows that the stated objectives were not generally achieved. The typical approach in many of these studies had been to take as many samples as the budget would allow using "standardized" sampling and analytical techniques. At the end of the study period, the investigator usually attempted to analyze the data to see if it could be used to gain inference on water quality in the region of the Great Lakes under investigation. This approach often failed to consider the variability of the system and, more importantly, the factors controlling it.

There are still far too many governmental, industrial and university scientists and engineers who, judging from the studies they have conducted, believe that some data on water quality parameters are better than none at all. This is a fallacious belief that may lead to significant errors in the development of management policy.

In the water quality area, it has been found that poor quality studies are being used by pollution control agencies as a basis for implementing environmental quality control programs. There are several notable examples of this with respect to the establishment of management policies for the Great Lakes and other waters. One factor contributing to this is that legislators exert political pressure on funding agencies to fund studies which may not necessarily have been originally well-conceived; this promotes the conductance of studies which, in the opinion of the greater part of the technical community, are not technically valid. Normally, although not always, the results of a poorly planned and conducted study will have little or no impact on Great Lakes water quality management other than having wasted the funds that supported the project.

Another significant factor contributing to this situation is the recent large-scale reduction in funds available for Great Lakes water quality studies and monitoring. It is
likely therefore that in the future, as it has been in the past, that funding will be reduced over that originally proposed. This could lead to situations where it would be impossible to properly conduct originally well-conceived studies. If the investigator proceeds with the study under conditions which he/she knows will generate inadequate data in order to achieve the original objectives, rather than redefine the objectives or not conduct the study at all, this may lead to the development of conclusions that have an insufficient data base that could have a significant influence on management policy.

Since water quality management policy in the Great Lakes represents expenditure of very large amounts of public funds, a concerted effort must be made to see that these expenditures are responsible for the generation of sound technical data. It is imperative that those responsible for funding of research designed to develop information for water quality management in the Great Lakes develop a more effective means of screening projects prior to initiation and therefore avoid the above problems. The researchers must become more effective in informing those responsible for funding of these projects that small amounts of money often lead to situations which may be worse than having no information at all. This paper presents an approach that should be considered in any Great Lakes water quality study and, hopefully, will serve as a guide to the investigators, research managers and those responsible for funding of research; if followed, it will help to improve the quality of research results and maximize the information gained from the funds expended.

SPECIAL CHARACTERISTICS OF THE GREAT LAKES

Water quality study and monitoring programs for the Great Lakes require that consideration be given to three distinct regions. These regions are the open waters, near-shore waters and harbors or restricted circulation areas.
The characteristics of each of these three regions as they influence water quality study and monitoring programs are discussed below. The IFYGL studies of Lake Ontario during 1972 provide a unique data base for the Great Lakes on the characteristics of tributary rivers, and of nearshore and open waters of the lake. Lee and Jones (1979) provide a detailed discussion of the characteristics of these waters for selected contaminants investigated as part of the IFYGL.

OPEN WATERS

The open waters of the Great Lakes represent the bulk of the water in the lakes. These waters generally extend to within a few kilometers from shore. At times, due to meteorological conditions, these waters can be immediately adjacent to the shore. The open waters are often studied in Great Lakes water quality studies; yet, these same waters are rarely seen by the public. The public is primarily concerned, however, with the nearshore and harbor waters as opposed to the open waters, since it is the former which it generally uses for water supplies and recreation.

The open waters of the Great Lakes generally have lower concentrations of contaminants than do the nearshore regions. Generally, these waters are reasonably well-mixed compared to the other regions during the fall, winter and spring. During the summer, thermal stratification divides the lakes into two-layer systems which, dependent on the aquatic plant nutrient load, may cause significant vertical differences in the concentrations of many water quality parameters.

Sometimes, individuals in water pollution control agencies maintain that waste input to the lakes must be curtailed even though detailed studies of the lakes fail to show any measurable concentration increase in water and organisms or the effect of these inputs. These views are related to the fact that, at the present time, the Great
Lakes are, to some extent, judged according to experience with smaller lakes, rivers and estuaries. In such bodies of water, moderate wasteloads produce excessive concentrations of contaminants and the concomitant detrimental effect on water quality. The Great Lakes, however, have a large waste assimilative capacity, which means that wasteloads for certain types of contaminants can be significantly higher than in smaller lakes without causing a measurable increase in concentration of the contaminant in the system or any significant deterioration in water quality. It is important to emphasize that, for many chemicals and other contaminants, the effect on water quality is based on concentrations and not on total mass input. It is only when the concentrations of available forms approach or exceed a critical value for certain types of water use, that significant efforts should be made to curtail the input of difficult-to-remove contaminants.

There are certain types of chemical contaminants, however, for which an extremely conservative approach must be taken with respect to their discharge to the Great Lakes. Highly persistent chlorinated hydrocarbon pesticides and PCB's have accumulated in Lake Michigan fish to the extent that their concentration in these fish exceeds the action level of the FDA designated for fish used as human food. The primary problem arises from their long term stability and availability in Great Lakes ecosystems and the very high bioconcentration of these compounds from water.

Because of the very low concentrations of contaminants actually present in the "soluble phase", it is often necessary and essential to include in any open water monitoring program the measurement of contaminant levels in fish or other groups of aquatic organisms. These organisms are integrators of the environment and therefore, as a result of bioaccumulation, tissue analysis may be the best method of detecting potential water quality problems in the open
waters of the Great Lakes for many contaminants which tend to persist and accumulate in aquatic organisms and terrestrial animals, i.e., birds, that utilize aquatic organisms as a source of food before excessive concentrations accumulate within the organisms.

Studies of the open waters of the Great Lakes require large-scale funding for ship operation if an adequate number of samples are to be obtained in order to properly define general open water quality-related content for a particular contaminant. Funding of open water quality studies on the Great Lakes with "rowboat budgets" is one of the primary reasons many of the previous studies have failed to yield significant amounts of data which can be used to define water quality in the open waters.

Because of the very high expense associated with comprehensive water quality studies of the Great Lakes, a series of reference stations should be established in the Great Lakes' open waters. The recent significant reductions in Great Lakes research and monitoring funds makes this approach mandatory. These stations should be carefully selected and their placement based on extensive studies of the relationship between the water quality at the stations and in the bulk of the open waters in the immediate area and on the currents in the lake near the major contaminant inputs, such as urban centers. There should be specific areas of each lake where open water reference stations would detect significant changes in contaminant levels before general buildup occurs in the open water ecosystem. The reference station should be sufficiently distant from contaminant sources so as to minimize the high variability levels that are associated with proximity to most contaminant inputs. Open water reference stations should be sampled at monthly or more frequent intervals. On the Great Lakes, general intensive lakewide sampling studies of the IFYGL type should be done at a minimum of 10 year intervals.
in order to check the reliability of the reference station results.

NEARSHORE AREAS

The nearshore waters of the Great Lakes, as well as of other bodies of water, are often of significantly different composition than that of the open waters. In small water-bodies, such as small lakes and rivers, the band of water near the shore, which has very different water quality from that of the open water, is often very narrow and rarely studied. In the Great Lakes, the nearshore waters form a more or less distinct entity promoted primarily by the strong shore currents. While it is sometimes said that the thermal bar is a cause of the buildup of contaminants in nearshore waters of the Great Lakes, it is doubtful that, based on the available data, the thermal bar plays any significant role in trapping contaminants in the nearshore waters.

The nearshore waters of the Great Lakes are the waters that have the greatest impact on man. Few studies, however, have been conducted by pollution control agencies on these waters because of many factors, one being that it is more difficult to study this area than to study either the open waters or the harbors. There are also political factors contributing to the paucity of studies on nearshore waters; the nearshore zone often represents a boundary between state or provincial government and the federal government. Therefore, one group works to the lake's edge and the other on the open waters with few, if any, studies conducted at the interface.

The nearshore zone, in addition to being the region of the lake which has the greatest impact on man's water supply and recreational use, is the nursery area of the lake's ecosystem; reproduction of many of the higher animal forms takes place in this area. Since this area generally has higher concentrations of contaminants than do the open
waters, the most sensitive forms, i.e., larval forms, of some aquatic life are exposed to some of the adverse conditions in these waters.

Except for atmospheric inputs, which are significant for the Great Lakes with respect to many contaminants, man's activities result in a higher contaminant concentration in the nearshore zone as the result of wastewater inputs and of agricultural, forest and urban drainage. It is important to point out that the higher concentrations of contaminants found in nearshore waters may not necessarily be adverse to the lake. The nearshore waters are subject to potentially significant mixing of water and sediments. This zone also receives the particulate forms of contaminants from wastewater inputs and runoff. This results in higher concentrations of particulate forms of many contaminants in the nearshore waters than in the open waters of the lake; however, these forms may not be adverse to the lake's ecosystem because of their greatly reduced availability to aquatic life. This means that caution should be used when utilizing water quality standards based on dissolved species, i.e., applying open water conditions to nearshore waters, since often the bulk of the contaminants in the nearshore waters may not be in a form which could be adverse to aquatic life. There is a need for study directed toward establishment of water quality criteria for particulate forms of contaminants. Lee et al. (1976) presented a comprehensive review of the potential significance of sediment-associated contaminants to water quality. A summary of the results of comprehensive studies on the significance of contaminants associated with U.S. waterway sediments has been recently published by Jones et al. (1981).

In addition to generally having higher concentrations of contaminants, nearshore waters also tend to have a much more variable composition. This variability is influenced by both the land input patterns and the hydraulic
characteristics of the lake. The physical boundaries of the nearshore zone are highly variable, defining a zone width ranging from essentially zero, i.e., when open waters are completely mixed to the shore, to a width extending several kilometers from shore. Factors such as wind intensity, wind duration and direction, lake bottom and shoreline morphology, etc. determine the nearshore zone characteristics. The direction and magnitude of the current are also highly variable. These factors make the establishment of an appropriate reference station in the nearshore zone a difficult task because any station that is established would tend to get higher levels of contaminants, when the currents carry the waters from the nearby urban center to the station, than those measured out in the open waters. A considerable amount of work needs to be done on the feasibility of establishing reference stations in nearshore waters. It is highly desirable to be able to detect significant changes in contaminant levels in the nearshore zone. There is a possibility, however, that the noise levels associated with a high variability of the concentrations in the nearshore waters may make the use of reference stations in this zone extremely difficult, if not impossible, without high levels of funding.

Water supply intakes are sometimes used in attempting to monitor water quality in the Great Lakes. There are some notable examples of data sets obtained from water supply intakes, such as the phytoplankton data from the Cleveland water supply intake (Davis, 1964). Also in this category is the Chicago water supply intake data for the phosphate concentration found in southern Lake Michigan reported by Vaughn (1970). Examination of these data reveals a high variability in the chemical characteristics of southern Lake Michigan water. These data readily demonstrate the variability of these waters as discussed above. Many of the water supply intakes on the Great Lakes are located on the
shore; others are several thousand meters from the shore. Water depths sampled vary from surface to several tens of meters below the surface. Offshore intakes may be located at or near the boundary between the nearshore and open water. The classic studies of Mortimer (University of Wisconsin, Great Lakes Institute, Milwaukee, Wisconsin) on the temperature variability of the water supply intakes on Lake Michigan show quite marked temperature changes (ranging up to a few degrees in a few hours) associated with internal standing and progressive waves.

At one time the intake is taking epilimnetic waters; a few hours later, it is taking hypolimnetic waters. This situation would prevail for a finite period of time each year. The fact that the water supply intakes sample water from different water masses could cause difficulties in data interpretation; however, if the data are normalized or categorized according to temperature or some other characteristic that is indicative of water mass, information could be gained that would give the characteristics of each water type from a single intake. The use of water supply intakes as reference stations for nearshore epilimnetic, hypolimnetic and open water characteristics is an area that needs further study in order to evaluate their potential role as monitoring stations.

Contamination from intake pipes and pumps is essential to keep in mind with respect to the use of water supply intakes as reference stations. Unpublished results of the authors have shown that the zinc content of Lake Michigan nearshore waters, as measured by a water plant intake, is markedly different from the actual zinc content in the nearshore waters near the intake. This is a result of zinc contamination in the intake pipeline. Similarly, caution must be used when sampling the nearshore waters through intake works when the water has not been free flowing for a period of time. Many water supplies take water for limited periods
of time. If the sampling is done under conditions where the pumps have not been running to a sufficient extent so as to pump out the water that has lain in the pipe, nearshore water characteristics could be found which actually reflect waters in the pipe and not necessarily the nearshore waters of the system.

Sampling of the nearshore waters presents a problem in that it is possible to use a "rowboat budget" approach or even a rowboat for actual sample collection. Using vessels of limited seaworthiness for sample collection in nearshore water necessitates sampling in calm water. It is essential that ships of great seaworthiness be used to sample waters during periods other than calm weather in order to gain information on water quality characteristics during these times. It is possible that when there is mixing of the sediments with the overlying water that there would be markedly different water quality characteristics than those determined by calm water sampling only.

There are also problems with attempts to use too large a sampling ship for these waters. Deep draft vessels have a significant potential for grounding in some nearshore waters of the Great Lakes. Captains of such vessels are frequently very reluctant to go into waters where the draft of the vessel is within several meters of the water depth. Optimum sampling ships for the nearshore waters are of an intermediate size, between the typical oceanographic sampling ship and the 20 to 30 foot runabout or small cabin cruiser.

HARBOR AND RESTRICTED CIRCULATION AREA SAMPLING

There are numerous areas on the Great Lakes where the water quality is significantly different from that of either the open waters or the nearshore zone waters. These areas have very high waste input from urban centers located along the shore or inland on tributaries which discharge in the region. With few exceptions these areas, such as harbors
and river mouths, tend to have restricted circulation or exchange of water with the open waters of the lake; under these conditions, the highest concentrations of contaminants are found. The concentrations tend to be highly variable in these areas due to the variable input of wastewater sources and, in areas with significant tributary input, to riverflow and land runoff. To some extent, these areas can become mixed with the open waters during periods of high wind stress associated with storms.

Generally, these harbors or restricted circulation areas can be sampled with small boats and, therefore, are much less expensive to study; however, it is important to note that while these areas are of high public concern because of their proximity to urban centers, they rarely reflect open water conditions. It is possible that the high concentrations of contaminants which may cause potentially adverse effects in many of these areas could be diluted or reduced so that they would have little or no effect on lake-wide water quality; in fact, contaminants which may be important in this region may be totally insignificant in the lake as a whole.

An example of this situation occurs in southern Green Bay on Lake Michigan. Studies by Sridharan and (1974) have shown that phosphorus is not limiting in this area. The phosphate input from domestic and industrial wastewater sources and land drainage is sufficient, so that algal growth is controlled by nitrogen or other chemical species, or light. Predictions based on these studies are that removal of 80 to 90 percent of the phosphorus from domestic wastewaters entering southern Green Bay would have little or no effect on the algal problems in this area because the phosphorus contributions from other sources, such as land drainage and urban runoff, would be sufficient so as to maintain surplus phosphorus for algal populations. One would conclude, therefore, from a cursory examination of
the situation that phosphate removal is not justified; however, when Lake Michigan as a whole is considered, it is found that in mid-Green Bay phosphorus is once again limiting; algal growth here is dependent on the phosphate concentration. Thus, any attempts to remove phosphate from the inflowing waters would be of benefit to the lake as a whole.

Another situation demonstrating how restricted circulation areas may not necessarily reflect lakewide conditions is that of Cleveland harbor where studies show that algal growth is limited by a toxic component. It is conceivable that the treatment of domestic wastewaters by alum, lime or iron salts to remove phosphate could, at the same time, remove a significant part of this toxic component. As a result, algal growth in the bay might be increased upon phosphate removal, rather than decreased, if the technique removes a significant part of the toxicant and if a significant amount of phosphate is derived from other sources. This does not mean that phosphate removal should not be practiced at Cleveland harbor since, while it may be of little or no value in controlling algae in the harbor, it certainly would be of value to Lake Erie as a whole.

From the above discussion it is apparent that any attempt to use harbors or restricted circulation areas as a measure of potential water quality problems in the Great Lakes may meet with significant problems. Such studies should be very carefully reviewed before being granted any significant funding.

AN APPROACH TO THE STUDY OF GREAT LAKES WATER QUALITY

Presented below is a series of items which should be reviewed in any study that is contemplated for ascertaining water quality in the Great Lakes or, for that matter, any body of water.

1. **Clearly define objectives of the study.** One of the
most significant problems that exists today with the majority of water quality studies is the failure of the investigators to clearly delineate the objectives of the study and to then design the study accordingly. The objectives of the study must be defined in a clear, concise manner in order for a meaningful study to be developed. "Fuzzy" objectives like, "What is the water quality of Lake Michigan?", lead to a collection of miscellaneous data which are often essentially uninterpretable. Specific objectives like, "What are the current PCB levels of Lake Michigan fish?", lend themselves to clearly definable studies.

Not only must the objectives of the study be well defined, they must also be technically attainable. To set forth unrealistic objectives is as technically unsound as to conduct studies for which the objectives are poorly defined. One such unattainable objective is the attempt of some regulatory agencies to require large-scale studies on the whole of Lake Michigan in order to determine some of the subtle effects of using the lake's nearshore waters for once-through cooling at electric generating stations. The studies conducted thus far demonstrate that it is extremely difficult to show any adverse effects in the region of the discharge, much less in the lake as a whole, in a situation where a very small area of the nearshore waters is being heated a few degrees above ambient. Even if studies were to show widespread changes in the character of the lake proper, it would still not be possible to determine if these were due to natural variations in the system, municipal or industrial discharges, electric generating stations using once-through cooling or to other factors. In the opinion of the authors, attempts to detect lakewide changes due to thermal discharges in a system such as Lake Michigan represent unattainable objectives and will result in the expenditure of large amounts of funds for the development of possibly inappropriate conclusions without having achieved
the objective of the study.

2. **Determine the level of confidence at which the objective is to be achieved.** Once the objectives of the study have been delineated, the next step is to determine the degree of confidence that should be attained in achieving the objective. Is it sufficient to know the PCB concentrations in Lake Michigan fish at a 95 percent confidence level, 99 percent confidence level, or at some other value? It is important to note that for some chemical contaminants it cannot be assumed that their distribution in the population under study will follow a normal distribution. Tests of the population should be made to ascertain what the actual form of the distribution is; the statistical studies should be designed according to the distribution found. At the commencement of any study, it may be necessary to assume that there is a normal distribution. Then, once some data have been gathered, the sampling program may be adjusted according to the actual statistical distribution.

A special situation exists when the primary objective of the study is to provide information that can be used in formulation of public policy. In studies such as those directed towards determining whether a particular input of a chemical contaminant should be permitted, questions should be raised about the sensitivity of the decision-making process relative to the precision and accuracy of environmental "impact" information. For many public policy situations, the decision is relatively insensitive to the degree with which one defines the load-response cause-effect relationship.

Prior to initiation of the study, each investigator in a situation of this type should make some judgments as to the expected ranges of the final results and, for the extremes and intermediary values, determine what the public policy would likely be. With this information he/she should conduct a sensitivity analysis to determine how a change in public policy would be dependent on a change in
the results of the study. Based on this analysis, formulation of the degree of reliability that the study must achieve should be made in order to enable cost-effective formulation of public policy within the options that are potentially available.

3. Select the parameters to be measured and justify potential significance of each parameter selected. Once the objective of the study has been clearly delineated, it is then possible to determine what parameters should be measured in order to achieve this objective. Studies on water quality often take the "grab bag" approach, in which "everything" is measured. Instead, each parameter selected should be clearly justified in terms of its potential significance in achieving the objective of the study. The individuals who design the study should ask themselves how the measurement of each parameter can be used to achieve their objectives and how precise a measurement of the parameter is required. The latter question becomes important with respect to the level of confidence needed to achieve the overall objective.

Often, investigators tend to add parameters, somewhat at will, to the point at which a sufficient part of the funds available for the study have been devoted to measurement of peripheral parameters which in themselves might be of interest, but which do not contribute to achievement of the overall initial objective. If the study is designed to measure PCBs of Lake Michigan fish, then there is no point in spending large amounts of money determining the mercury content unless this is clearly delineated as an additional objective of the study. Careful scrutiny should be given to all parameters which are selected to be certain that they are within the scope of the project and that the individuals who designed the study can clearly justify their significance.

A special situation develops in connection with open water sampling in which a larger ship is used and a crew of
several technical people is available at each sampling location. Under these conditions, additional samples could be processed or additional parameters measured while the ship is proceeding from one sampling station to another. The cost of open water sampling programs is often highly dependent on ship time costs. A few additional chemical analyses or biological measurements would not add significantly to this cost and they could be justified from the point of view that the technicians are already available to perform the analyses and that the results of these analyses could be helpful in interpretation of the other data.

4. **Examine previous studies to establish variability in each area of the lake to be studied.** Far too many studies are conducted on the Great Lakes and other bodies of water without careful review of previous studies. The data collected in previous studies, even though inadequate to achieve the objectives of the present study, can still be of significant value to present and future studies by helping to define the variability of the system. If one wants to know how many samples are needed to determine the zinc content within a certain degree of reliability in the open waters of one of the Great Lakes, examination of the previous studies on zinc in these waters can be a useful guide for determining the proper number, depth and location of the samples. It is important that any review of this type clearly delineate between the three regions of the lake discussed above and do not mix data from open waters, harbors and nearshore waters as these are distinct regions which require separate treatment.

5. **List factors that can influence results of studies.** Often in studies, samples are collected and the data are analyzed to see if they reveal anything about the characteristics of the system. This type of program frequently utilizes an arbitrary sampling scheme that does not make
use of the information available on the system. The Great Lakes, as all other waterbodies, behave according to certain fairly well-defined principles of physics, chemistry and biology. While these principles may not be fully understood, there is considerable knowledge about them which could be used to develop a more efficient study program.

For example, if one is interested in the potential significance of the thermal bar as a barrier to the transport of chemicals from nearshore to offshore water, one would not measure only the surface water characteristics at the thermal bar as has been done in the past. An elementary understanding of the physics of the thermal bar shows that it is a zone of intense mixing of the inshore and offshore waters. Marked differences would be expected in the surface water characteristics across the bar. However, if one measures vertically at the bar one finds that these differences disappear as a result of mixing processes and that there would be significant transport of nearshore contaminants to offshore waters at the "bottom" of the bar. Any sampling program must include both horizontal and vertical sampling on each side of the bar in order to understand this transport process.

If the objective of the study is to determine the total flux of a chemical contaminant in a particular tributary to a certain part of the Great Lakes, one should not establish a sampling program that grabs samples every two weeks, every month or some other arbitrary period. The sampling program should be established based on the mass transport relationships that exist for that contaminant. For example, for contaminants that tend to be associated with particulate matter, sampling a few days per year during the periods of high flow may give a better estimate of the total flux than sampling every Monday for a full year. It is important to note, however, that, as discussed by Lee and Jones (1978), the sampling of high flows when maximum suspended transport
takes place, while providing a better estimate of total contaminant load, does not necessarily provide information on the contaminant load that controls water quality in the receiving waters as a result of the fact that much of the particulate-associated contaminants are unavailable to affect water quality. It has been found for many chemical contaminants that the concentrations in a particular stream or river are highly dependent on discharge rate. Therefore, sampling programs which do not consider discharge as the driving force often lead to incorrect conclusions with respect to the total mass transport of the parameter.

Pickard (1963), in a paper presented at the Great Lakes Conference, demonstrated that an arbitrary sampling program in which samples are taken at some predetermined frequency, ignoring the factors driving the system, could yield incorrect results for changes in concentration in the parameter over a given time period. All readers should review Pickard's paper before establishing any sampling program.

In designing a water quality monitoring study, one should ask oneself, "What factors will influence the results and how should the study be designed in order to evaluate the significance of these factors?" Once this has been done, it is likely that some additional sampling should be carried out in order to make measurements at certain critical times and locations. The behavior of water quality contaminants in natural water systems is often controlled by certain meteorological, chemical or biological events. The sampling program should reflect an understanding of these events in order to be able to account for why a particular concentration of a contaminant is found at a given location on a certain date. In this way it would be possible to ascertain, the next time that sampling occurs, whether the differences in contaminant concentration between the two dates are differences related to a natural driving force or are resulting from man's activities.
The best approach in formulating the relationship between the contaminants and a driving force is to construct simplified models which describe the system. While no attempt may ever be made to develop these models to the point where exact mathematical formulations would be used, the modeling process is often useful in formulating studies in order to focus on what are thought to be the key factors controlling the system.

6. For each area of the lake to be studied, determine the number and location of samples to be collected. Only after the steps in Items 1 through 5 above have been taken, can the investigator begin to develop meaningful sampling programs to achieve a certain degree of understanding of water quality in the Great Lakes. Particular attention should be given to designing the sampling program according to the variability of the system (as discussed in Item 5 above). The sampling locations, both with respect to horizontal distance and vertical depth, should be designed to reflect the overall dynamics of the system and the factors affecting variability.

After critical examination of the information listed above, determine the numbers, types and locations of samples in order to meet the study objectives. It is usually wise at this point to have the study plan reviewed by outside experts who can determine whether the investigator's approach is valid. Frequently, preparing the study plan in sufficient detail so that it may be examined by someone not previously acquainted with the particular study, but who is competent in the study topic area, can prove to be of significant value to the investigator since preparation for such a review will often elucidate problems in the study plan. Further, frequently outside consultants who have conducted similar studies on other waterbodies can detect potentially significant problems in the study plan. Conducting such a review, therefore, is highly cost-effective with respect to
improved quality of the results of the study.

7. **Conduct a pilot study if no data from a previous study are available.** In some instances, no data will be available from a previous study on a particular water quality characteristic of the part of the Great Lakes under study. In these instances, it may be necessary to conduct a pre-study or pilot study in order to gain some information on the factors controlling the system and its variability. This pre-study may require several weeks to several months to complete. At the end of this time, it will be possible to design the overall study according to pre-study results. In order to design the pre-study, one should consider similar studies that have been conducted on other bodies of water. The approach utilizing a pre-study was designed into the Wisconsin Department of Natural Resources' thermal pollution studies on Lake Michigan (Lee, 1972). A similar approach should be used for chemical and biological contaminants.

It is important to note that a pre-study of several months' duration may not be adequate to fully delineate the variability of the system, especially seasonal variation. Often, water quality characteristics of the Great Lakes and other bodies of water are seasonally dependent, therefore, a pre-study conducted in one season may not be adequate for other seasons. The study program may have to be adjusted to take into account changes that are observed as a result of the more intensive studies of the system.

8. **If the purpose of the study is to determine changes in water quality, select the magnitude of change that is to be detected.** One of the most frequent objectives in water quality studies is that of detecting whether or not a change in the chemical or biological characteristics of a given body of water has occurred over a certain period of time. In order to design a study for this purpose, it is necessary to select the magnitude of change thought to be of significance and to design the study accordingly. The magnitude of change in
concentration units is highly dependent on the relationship between the ambient concentrations and the critical concentrations for the body of water. For example, a several mg/l change in the total salt content of a body of water could be judged significant with respect to certain parameters of water quality. However, a doubling of the concentration of a trace constituent such as mercury, which exists at concentrations considerably below the critical thresholds established for aquatic life or bioconcentration, may not be significant. The establishment of the critical concentration change in a particular study requires a thorough understanding of the significance of chemicals to organisms and to water quality and a knowledge of the existing ambient levels of these parameters. Selecting the magnitude of change that is to be detected in any study designed to ascertain changes in water quality with time is a key process in designing a meaningful study. It is only in this way that one can determine the number of samples needed in order to detect this change.

Far too often, studies which are conducted on water quality in the Great Lakes and other waters conclude that there is no significant difference between the samples taken at some time previously and those of the current sampling program. By examining the results of these studies in detail, one finds that the primary reason for this conclusion is that the number of samples taken, either previously or currently, was insufficient to detect a potential change in water quality of a magnitude thought to be significant in the system under study. Rather than setting up a study program in which data are collected and then analyzed, one should establish a definite program which is carefully designed to test a specific hypothesis; the data are then collected according to a program built around proving or disproving this hypothesis.

9. Select sampling techniques and methods of analysis
in accord with the objectives and level of confidence desired. When the objective of a study is to determine the characteristics of water quality within a known degree of reliability, it is possible to utilize sampling techniques and analytical techniques designed to fit into this objective. As noted above, there is no point in measuring a particular chemical parameter to four or five decimal places when, in fact, one cannot ascertain the significance of a change in the parameter in the first whole number. In reviewing the sampling and analytical techniques, one should ask oneself, "What magnitude of change would be significant and how do the planned sampling and analytical techniques relate to this magnitude of change?"

It is important that the investigator ask what degree of precision and accuracy can be obtained with a particular sampling technique at a particular location. If he/she cannot answer these questions, then he/she should conduct studies in order to obtain this information as part of the overall study.

10. Check analytical methods for each area at various seasons to be certain they are applicable to the system under study. One of the greatest problems with many of the studies on water quality in the Great Lakes is that individuals do not check to be certain that the analytical methods they have chosen are applicable to the system they are studying. Far too often in the water quality control field, a "standard methods" procedure is selected, such as the APHA et al. (1981), the US EPA standard methods or the ASTM standard methods in order to make various chemical and biological measurements associated with the study program. A justification of this approach stems from the fact that many of the individuals using this method do not have the technical background to properly evaluate it. Secondly, they have the mistaken idea that even if the method does not yield accurate results that, since it is a standard method,
it should yield results which are comparable to another investigator's results. This is what the authors term the "Standard Method Syndrome". Using one method to obtain results comparable to those of another investigator does not relieve one of the responsibility of checking the reliability of the method in the system under investigation. Anyone familiar with Standard Methods (APHA et al., 1981) knows that with almost every edition there are changes usually improving the method for a particular analysis. Often these improvements are associated with the elimination of interferences in the method. The primary reason why a standard method may not yield comparable results is that one water could contain an interference which would completely invalidate the method, while another water could have a different amount of interference or even no interference at all. Therefore, results on the two different waters, even though the same analytical procedure has been used, are not comparable since they are a function of the amount of interference present.

In general, standard methods for water quality monitoring from various agencies or organizations should be used only as a guide to the selection of analytical procedures that have been found to work in a wide variety of waters. The investigator is responsible for conducting the tests necessary to be certain that the method is applicable to the particular waters under investigation. Generally, standard methods will work for open waters of the Great Lakes with little or no difficulty. However, in nearshore waters, particularly in the regions of urban centers and harbors, the increased concentrations of many interferences are such that the standard methods procedures may not work without modification.

Laitinen (1973) has presented a comprehensive review of the procedures that should be used in selecting an analytical procedure. The reader is referred to Laitinen's
review for further discussion of this topic.

In addition to selecting the sampling techniques and analytical methods, the investigator should also select the methods that will be used for the preservation and storage of the samples. Again, as with the analytical methods, the investigator should determine whether the methods selected are adequate for the particular study. One should not assume that because someone else has reported a chemical or condition as a suitable preservative for a certain parameter, that this would be applicable to the investigator's situation. Frequently, individuals ask how many samples should be taken, what analytical methods should be used, what preservative should be used, etc. The answers to these questions can be found by selecting procedures that have proven to be satisfactory for other waters and then evaluating whether these procedures are adequate for the particular system under investigation.

11. Conduct studies to evaluate sampling and analytical procedures and variability of system. A special purpose sampling program should be designed to evaluate the variability of the system for all three regions of a lake under conditions likely to be encountered (e.g., nearshore waters under storm conditions, open waters under calm conditions, nearshore waters during fall, winter, spring, summer, etc.). A set of replicate samples should be taken at the same time; a single sample which could be split into a number of sub-samples should also be used. These samples should be analyzed at the same time for each of the parameters under investigation. These results should be reported as part of the overall results to give the reader an indication of the precision that exists in the sampling and analytical procedure. Ten replicates often gives a reasonable estimate of the variability of the system at any one location. These studies should also include short term sampling over a period of time in order to check the variability as a function
of time. The purpose of this sampling would be to sort out high frequency variability that would be associated with certain types of limnological phenomena, tributary flow characteristics and wastewater inputs. It is important that studies of this type be conducted at the various seasons and under the various meteorological, limnological and other conditions that are encountered in the study area. One cannot assume that the results obtained in the variability study based on 10 samples during the spring would be applicable to other seasons. This type of information is essential in interpreting the results. If replicate sampling at one site is found to yield results with a certain standard deviation, then there is little point in trying to interpret differences between sites at which the numbers of samples taken are inadequate to account for the variability of the system at one site.

Some of the greatest problems of the type described above occur in benthic sampling of the Great Lakes and in other waterbodies. Frequently, samples are taken with a certain type of sediment grab in which one or two samples are taken over considerable distances in the Great Lakes. The investigator then attempts to utilize these data to develop inferences about the numbers and types of organisms and/or the physicochemical characteristics of the sediments at various locations in the study area. Actually, if the investigator had sampled at a particular site with repeated sampling it would have been found that a much larger number of samples was needed at one site than was used in his total sampling program in order to define the characteristics of one site, much less the differences between sites. For example, in a study in which the author has been involved concerned with the sampling of benthic fauna in Lake Superior, it was shown that in order to get an accurate assessment of the benthic population at a particular location in the lake, over 200 sediment grabs would have to be taken.
at one site.

The problems of sampling benthic organisms are greatly aggravated in the nearshore area. Often, extreme differences are found in the concentrations of various benthic organisms within relatively short distances. The same types of problems apply not only to benthic animals, but also to benthic plants such as Cladophora. There is need for a study on the Great Lakes in order to define how to sample Cladophora with a known degree of reliability in order to assess the reliability of remote sensing techniques for Cladophora measurements.

It is important to emphasize that in certain environments, especially sediments, repeated studies may have to be made during the course of the study of the variability of each of the major sampling sites and then the number of samples collected at any one site adjusted accordingly. This is especially true when high flow or other events have taken place. For example, in studying the environmental impact of dredged material disposal on benthic organisms in the Great Lakes, it is reasonable to expect that the number of samples needed at any one site to define the numbers and types of organisms present at that site, pre- and post-dredged material disposal, would be different. Often, the sediment character after disposal is changed from that of predisposal conditions, with the result that a sampling scheme established on the variability of the system prior to disposal may be inadequate for postdisposal conditions.

In addition to performing analyses on replicate and split samples, a well-defined appropriate quality control program should be initiated as part of the study. This program should include check samples in which knowns are run through the procedure at frequent intervals. Also, the standard addition technique should be used. In this, a known amount of the parameter under investigation should be added to the samples in order to determine whether recovery
of this added amount is obtained. The US EPA Handbook for Analytical Quality Control in Water and Wastewater Laboratories is recommended as a guide to a potentially suitable quality control program for environmental studies (US EPA, 1979); also APHA et al. (1981) contains useful information in this area.

In addition, standard samples should be processed; these are samples which are made up to resemble the water by an independent group. It is important that these samples have concentrations near those that are likely to be encountered. Considerable care should be given to developing the standard samples in order to prevent the results from reflecting the conditions within the standard sample which are different from those in the natural water under study. Particular attention must be given to methods of standard sample preservation and to the forms of the chemicals present in the standard sample.

The use of standard samples among various laboratories investigating a particular waterbody must be made early in the program and at frequent intervals during the course of the study in order to try to eliminate the significant differences that may exist between study groups. There have been Great Lakes studies in which several standard samples were run during the course of the study where significant differences were found among the various study groups. However, at this time, it cannot be ascertained whether these differences were real or whether they were due to operator error which occurred at the time of the processing of the standard sample. If this procedure is not followed there may be more difficulty in interpreting the results of the standard sample studies than the overall results of the lake study itself.

12. Critically examine the relationship between present and past sampling and analytical methods. A review of the past water quality data collected on many waterbodies shows
that, in general, the previous investigators used different analytical procedures from those being used today. As noted above, there are often significant differences between analytical procedures for the same parameter. This can cause problems with trying to relate the results of previous studies to those of current studies. One of the ways to investigate the potential relationship between two sets of studies, conducted at different times with different analytical procedures, is to perform analyses on the water with both analytical procedures and compare the results of the two. In some instances, it is possible to develop correlation factors between one procedure and another and therefore to salvage the old data to some extent; however, this procedure is not without its pitfalls. For example, if the previous analytical procedure was in error due to the presence of an interference in the water at that time or if an interference is present now that was not present at the time of the previous study, then running analyses with both analytical procedures would not yield comparable results.

A similar problem of this type relates to plankton sampling. Many of the early investigators utilized plankton nets to collect plankton samples on the Great Lakes. More recently, investigators, in an attempt to relate the changes in plankton populations in the Great Lakes over the years, have used similar nets. Unfortunately, this does not yield comparable results unless exactly the same numbers and types of organisms were present in the past and current studies. It is well-known that plankton net trapping efficiency is a function not only of the type of organism, but also of the total number trapped.

13. Analyze data as collected. In the vast majority of water quality studies on the Great Lakes and other waters,
data are collected for a fixed period of time, which is usually one year, and then a year or more is utilized for sample processing and data analysis. This approach is what Lee and Jones (1980) characterize as "passive" study and monitoring programs. In some instances, this approach is required because of the magnitude of the analytical program. However, for many physical, chemical, and biological measurements it is possible to process the samples immediately after collection; in fact, it is often mandatory that this be done because of problems related to sample preservation. Under these circumstances, the investigator should analyze the data as they become available and then adjust his sampling and analytical program according to the results obtained. It is relatively simple today, with the computer techniques available, to establish programs which would automatically screen all data put into the data bank in order to ascertain whether or not they are within the normal variability expected for the particular water of the system being investigated. Lee and Jones (1980) characterize this approach as an "active" study and monitoring program. This screening process should flag any outlying values for the investigator and force review of the data in order to be certain that there are no problems in either sample collection or analysis or data entry. If it is ascertained that such a problem does not exist, then a special purpose study should be conducted in order to determine why the samples are outside of the expected variability range. If a significant number of samples of this type occur it may be necessary, in fact mandatory, to adjust the sampling program in order to gather the number of samples needed to obtain a statistically reliable result. It must be remembered that the preliminary assessment of the variability of the system is usually based on a limited number of samples. It should be possible to adjust the sampling program during the course of the study to enable one to gain the maximum
information for the funds being expended.

It is often helpful to screen data with respect to trends either in space, time, or depth, in order to sort out outlying values. Generally, limnological data proceed in a certain reasonably well-defined manner in either time or space. An experienced investigator can examine data and determine whether or not they fit outside of these normal relationships. If this type of event occurs frequently, then special studies should be conducted in order to ascertain why such events occur. For further information concerning "passive" and "active" study programs, consult Lee and Jones (1980).

14. Analyze and interpret data. One of the major problems associated with large scale studies on the Great Lakes by governmental regulatory agencies is that often these agencies do not make sufficient funds available so as to enable an investigator to properly analyze the data after collection. There are several examples of regulatory agencies spending many millions of dollars collecting data on the Great Lakes which, some 10 years later, still have not been analyzed. This situation frequently occurs because even though the regulatory agency allocates adequate staff for data collection and processing, during the following year when the data analyses are supposed to occur, the staff finds that they have to spend time on some new problem and, therefore, they do not have adequate time to properly analyze the data. It is essential that anyone who utilizes public or stockholder funds for the purpose of data collection on water quality in the Great Lakes spend the time to properly analyze and interpret the data and publish them in a readily accessible place. Also, this data analysis and interpretation should include a comparison to the results of other investigators and a discussion of the possible reasons for differences between the various investigations.
As data are collected, emphasis should be placed on determining whether or not the various parameters that measure somewhat related characteristics of the lake are showing the same trends. Many water quality parameters behave in a similar way with respect to certain types of driving functions. It is important that any studies on water quality parameters determine whether or not the parameters are exhibiting normal behavior; if the examination of the data shows that they are not, then special purpose studies should be conducted to ascertain why this is the case.

Some investigators attempt to interpret the results of water quality studies through what is best-termed, "an excessive dependence on statistical techniques" such as correlation coefficients, etc. Statistical techniques should not be used as a crutch which serves as the sole basis for data examination and interpretation. An experienced investigator can readily ascertain whether a particular relationship is valid based on examination of the total data collected rather than by simply determining a correlation coefficient between two parameters. It is often possible that two parameters may show high degrees of correlation, yet this correlation would be judged spurious or insignificant based on the examination of other parameters. Properly collected water quality data often show high degrees of internal consistency among various parameters. An investigator should make use of these relationships in interpretation of the data collected in any particular study. Statistical techniques should be used, where appropriate, to aid in data interpretation. High degrees of correlation should never be interpreted as cause and effect. Frequently, many water quality parameters vary in the same direction with time leading to high degrees of correlation between several parameters which is not necessarily an indication of a cause and effect relationship.

Frequently in interpreting water quality data, problems
are encountered associated with the use of various statistical terms, such as "statistical significance". Often, reports from water quality investigations will discuss the data in terms of a statistically valid or significant relationship between two or more parameters; such a finding should not be automatically interpreted as a significant effect on water quality. Water quality is generally controlled by the concentration of a particular contaminant or combination of contaminants. The measurement of the tendency of a contaminant to be released from sediments or of the total mass input from a tributary cannot be interpreted with respect to the impact on water quality unless the actual mass transfer input results in the concentrations of contaminants in chemical forms which impair beneficial uses of the water.

Interpretation of chemical data for hazardous chemicals is rarely done properly. None of the conventional statistical parameters such as a mean, mode, median and standard deviation provide the kinds of information needed to properly describe a particular data set. The problem is that organisms are adversely affected by certain concentrations of chemicals over certain periods of time. Relatively large concentrations of toxicants can be present for short periods of time, whereas for extended periods of exposure, concentrations which do not have an adverse effect are frequently much lower. For many situations a factor of 100 exists between the chronic safe level and the 96-hour acute lethal level; however, very little information is available for the exposure duration-critical concentration relationships for times other than 96 hours or for chronic exposure. It would be inappropriate to require that every sample taken of the Great Lakes water have contaminant concentrations less than the chronic exposure safe limits established by a water pollution regulatory agency, such as the Quality Criteria for Water released by the US EPA in 1976 (US EPA,
1976) or the IJC Water Quality Objectives for the Great Lakes. In general, these criteria are based on chronic exposure situations; there is no doubt that exposures to concentrations considerably greater than these may take place without having an adverse effect on water quality and on aquatic life in Great Lakes waters provided that the duration of exposure is less than the critical time for that concentration. It is important to note that the critical time-concentration relationship is dependent on the life stage of the organism. An exposure of a certain level and duration may be critical at one time of the year and not at another.

In order to properly interpret chemical data, an understanding is needed of the relationship between the duration of exposure to certain critical concentrations of contaminants and its effect on organisms for various types of aquatic organisms and contaminants. For example, for what period of time can the various species of fish be exposed to levels of contaminants 10 times the chronic safe level established by the US EPA or the IJC and still not have an adverse effect on their growth, reproduction or use as a food for other organisms and man? Until information of this type is available, it is going to be extremely difficult to interpret chemical data as part of any monitoring program of hazardous chemicals in the Great Lakes.

A frequency distribution of the concentration-duration of exposure relationships that exist in a given area of the Great Lakes should be established. This would enable those who are responsible for judging the significance of a particular concentration of a chemical contaminant to examine the time-concentration relationships that exist in the water versus any information that may exist on critical duration of exposure to various forms of aquatic life.

One of the questions which should be asked in connection with a proposed program for the study of water quality in the Great Lakes is, "What should be done if it is found that
there are inadequate funds available to meet the project objectives at the desired level of confidence?" It is recommended that the investigator not proceed with the study until he/she has redefined project objectives and levels of confidence to match the funding available. It is far better to do an adequate study in one area than an inadequate study in a large number of areas.

With increasing emphasis being placed on the development of more technically valid, cost-effective contaminant control programs, less reliance is being placed on the use of worst case water quality criteria, such as those developed by the US EPA as a basis for determining permitted point source contaminant discharges. In the past few years, approaches involving hazard assessment techniques have evolved which, if properly used, will develop the most technically valid, cost-effective approach for maintaining desired water quality in a particular waterbody. Lee et al. (1982) have described a hazard assessment approach that can be used for this purpose. It is recommended that in conducting future water quality studies and monitoring programs designed to investigate the potential impact of a particular discharge that a hazard assessment approach of the type described by Lee et al. (1982) be followed.

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Guidelines for sampling ground water

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Fundamental to proper sampling of well water to assess groundwater contamination is an understanding that the composition of water collected from a well is frequently a function of the extent to which the well was pumped (or bailed) prior to sampling, the length of time since water was last withdrawn from the well, and—in some instances—the method of sampling. This is a result of several factors. The ground water of an area frequently occurs in multiple strata or aquifers that contribute ground water to a well at different rates depending on the head, the permeability of the aquifer material, and other variables. Further, it is rare that the chemical composition of each aquifer-layer is the same; therefore, the composition of the water in a well that penetrates several aquifer-layers will almost certainly change, sometimes drastically, as a function of the length of time since the last pumping or sampling, or as a function of the length of time the well is pumped.

Ground water in areas near waste disposal sites is frequently anoxic and hence tends to contain high concentrations of soluble iron. This condition can result in variable concentration as a function of pumping. In standing water in a well open to the atmosphere, the dissolved iron will be oxidized to ferric hydroxide, which will precipitate and slowly settle in the well. Ferric hydroxide is an efficient scavenger of a wide variety of contaminants and would tend to cause the well water to have lower concentrations of many contaminants of concern than those actually present in the aquifer(s). It is very important in sampling ground waters to be certain that the water collected has the same oxidation-reduction and other chemical characteristics as the aquifers from which the water was derived.

Also potentially affecting the chemical characteristics of well water is the material used in constructing the well. Metal pipes can corrode and add metal to the water. Iron-containing pipe tends to leach iron, which could form ferric hydroxide and remove other contaminants from the water, as described above. Sometimes, relatively inert plastic pipe is used but with metallic, such as brass, well screens. These screens, especially in more acidic waters, tend to corrode, contributing copper, zinc, and other trace metals to the water. Although plastic is the most desirable construction material in most cases, plastic pipe can sometimes leach metals (such as zinc, used as plasticizers), as well as a variety of trace organics derived directly from the pipe, or various cement or bonding materials used to join sections of pipe. This situation further points to the necessity of pumping a well vigorously before sampling to ensure that the water collected does not contain foreign materials not representative of the aquifers being sampled.

It is important to realize that contaminants derived from waste disposal sites often do not mix rapidly with the water in an aquifer, but rather tend to move as a relatively thin layer on the surface of the aquifer, or—because of a higher density created by high salt content—near the bottom of the aquifer. This situation further contributes to changes in composition of water collected from wells as a function of the degree of pumping.

WATER SAMPLING PROCEDURE

When a new well is developed for groundwater sampling purposes, it should be pumped vigorously until the water appears free of suspended solids (SS). The well should be allowed to stand several days and then pumped again to flush it. If the water is clear (essentially free of turbidity), then the well sampling program can be initiated.

The proper approach for initial sampling of ground waters from a well is to collect a series of samples as a function of pumping time to define how long the well must be pumped (number of well volumes) prior to collecting a sample, to be certain that water collected is representative of the ground water. The sampling frequency to be used for this evaluation should be determined for each particular well. As a general guideline, a well should be sampled at 1, 2, 4, 6, and—if possible—10 well volumes during pumping. The well volume is estimated by the diameter of the well and depth of the
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Water in the well at the time of initiation of pumping. If the well is a low-yield well, it may become necessary to forego the higher well volume samples. If this is done, then it must be realized that the composition of the water in the final sample may still not be representative of the ground water in the region.

Each of these samples should be analyzed for the constituents of concern, as well as certain bulk chemical properties, such as specific conductance, temperature, and dissolved oxygen (DO). The specific conductance value provides valuable information on the relative contributions of waters from various aquifers in a particular well. If it is found that the specific conductance changes with duration of pumping, then it is almost certain that the concentrations of trace contaminants of interest will also be changing. The DO data are useful to indicate the redox state of the ground water. If the DO concentration of the water in the aquifers is less than about 1 mg/l, then the potential exists for ferric hydroxide to be precipitating and scavenging contaminants of interest when the aquifer water sample is exposed to the atmosphere in the well in the sample container, or during sample handling. If the sample contains dissolved iron concentrations of 0.01 mg/l or greater, than all sample collection and manipulation in the field and laboratory must be done so as to avoid exposing the sample to air. This precaution may be particularly important during the sample filtration step. It may be necessary to filter the samples in a glove bag under a nitrogen atmosphere.

Examination of the groundwater composition data as a function of well volumes pumped should show a leveling off to a plateau value with increasing well volumes pumped. At the well volume at which composition data values plateau, composition is independent of well sampling technique. If a plateau is not obtained, then great caution must be exercised in interpreting the groundwater characteristics data. Rather than being representative of the ground water in aquifers penetrated by the well that have not been sealed off, the measured groundwater composition is indicative of sampling, or sample holding techniques, or both, that make the data essentially worthless for water quality evaluation purposes.

Once it is established how long (that is, how many well volumes) a particular well needs to be pumped before a representative sample is collected, then—for future sampling—the well can be pumped for that number of volumes before sampling. An evaluation of the concentration-pumping duration (well volume) relationship should be made at least twice each year for 3 years for each sampling well (that is, once each spring-summer and again each fall-winter). This reevaluation is especially important for wells that are located in areas with widely fluctuating water tables where more frequent sampling program evaluation should be made in order to determine the extent of water table variations and their influence on the water composition-duration of pumping relationships. Depending on the year-to-year variability in concentration-pumping relationships during the first 3 years, it should be possible to decrease the frequency of reevaluation to every 3 to 4 years. The reevaluation can readily be done by collecting samples before and after the previously selected well volume flushing period.

The type of pump used in sample collection must also be evaluated to ensure that it does not alter the composition of the water. Gas lift systems can readily change the pH of the water being sampled by changing the CO2 partial pressure within the water. Further, gas lift pumping systems that have DO in the pumping gas, such as air or impure nitrogen, could result in the oxidation of ferrous iron to ferric iron, which—as discussed elsewhere in this section—has a marked impact on the forms and amounts of chemical contaminants in the water. The oxidation of iron can also affect the pH of the water through iron hydrolysis reactions, which can have an impact on the thermodynamics and kinetics of a wide variety of other reactions that can occur within the system. In general, gas lift pumping systems should be avoided because of these problems. If used, they must be carefully evaluated relative to mechanical and bailing methods. It should be noted that mechanical pumps and bailers should be made of plastic material or coated with plastic, and should be lubricant-free so as to avoid contamination of the water by the pump or bailer. Every pumping or bailing system considered for use should be evaluated for its potential to contaminate the water being sampled.

For certain types of pumps or bailers, it may be possible to use metallic apparatus when the rate of transfer of metals and other contaminants is sufficiently slow compared to the rate-volume of water being sampled, to avoid a significant degree of contamination. It should be noted that new pumps, tubing, and so on are particularly prone to releasing contaminants to water with which they come into contact. New apparatus should be soaked in water for at least a day, then thoroughly rinsed prior to use. One of the most notorious of such problems is caused by the zinc derived from plastics and rubber. Normally, the high release rate of zinc observed initially in these cases is rapidly decreased upon soaking.

Gibb et al.1 of the Illinois State Water Survey have a contract with the U. S. Environmental Protection Agency (EPA) to investigate monitoring with sampling and preservation techniques. Although at the time of preparation of their paper (1980) their work had only just begun, it is expected, based on the direction that the Gibb et al. study is taking, that these authors will soon be obtaining data that will demonstrate the various kinds of problems that are discussed in this section and that are generally known by those familiar with appropriate methods for groundwater sampling.

Information on procedures for collection and field

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analysis of groundwater samples for unstable components is provided by Wood. Also, the reader is referred to the *Groundwater Monitoring Review* (Lehr) for additional information on overall approaches that should be used in sampling and sample handling for groundwater quality monitoring.

**SAMPLING FREQUENCY AND LOCATION**

The groundwater monitoring wells should be positioned to monitor overall water quality characteristics of the ground water in the region, and both up- and down-groundwater hydraulic gradient from suspected specific sources of contaminants such as a waste disposal area, the sludge dewatering lagoons, contaminant storage areas, any sumps created to collect surface runoff, and so on. One or more up-hydraulic gradient monitoring wells should be drilled at the site. Several groundwater sampling wells should also be positioned along the property line of the site to properly define the character of the ground water entering and leaving the site. The wells should be drilled to a depth of approximately 3 m below the expected minimum annual water table for the region at that specific location. If the aquifer is more than 5 m thick, then it is recommended that a nest of three wells be constructed—to sample waters at about 1 m below the upper elevation of the aquifer, at mid-aquifer elevation, and near the bottom of the aquifer. The uppermost wells should be positioned so that their sampling points are always within the aquifer. For widely fluctuating water tables, this may require several aquifer surface wells. Some geological strata have high permeability layers of sand, sandy clays, and so on. Many of these layers are relatively thin. Any water-bearing layers of this type located near waste disposal facilities should have monitoring wells constructed to sample the water within the lenses.

Of particular concern at most sites are the nearby wells used for domestic and agricultural water supply. Such wells should be monitored as part of the overall monitoring program. The monitoring of the water of these wells and of the monitoring wells should be conducted at monthly intervals for 1 year to establish the variability of the composition. If the wells have reasonably constant compositions (that is, the concentrations in the well can be predicted with a reasonable reliability based on previously conducted studies), then the frequency of sampling during the second year can be reduced to quarterly. If the variability remains about the same during the second year, then the frequency of sampling can be reduced to twice a year in subsequent years. It may, with several years' records, be possible to reduce the frequency of sampling of monitoring wells of this type to once a year.

In addition to the overall monitoring wells of the region that are positioned along the upper and lower hydraulic gradient property lines for the site, plus existing wells in use near the site that could potentially be contaminated by the site's operation, it is desirable to locate several series of wells within relatively short distances of potential sources of contaminants (for example, the solid waste disposal area, sludge lagoons, and sumps for surface runoff collection). These wells should be set up to monitor ground waters passing through the potential site of contamination—both upstream and downstream of this site. The wells should be located a few meters from the area to detect groundwater contamination before it becomes a generalized problem of the area. These wells should also be sampled at monthly intervals and then at quarterly intervals after concentration-time patterns are established. It is recommended that the frequency of sampling at these wells not be reduced below quarterly so as to ensure that any problems of groundwater contamination are detected as early as possible. The monitoring wells for the specific contaminant source monitoring should be drilled 1 to 3 m below the area's annual low-water table position. The groundwater hydrology may necessitate the construction of nests of three wells of the type described above for peripheral site monitoring.

**MONITORING PARAMETERS**

In general, the following parameters should be measured on all well samples:

- **pH**
- **temperature**
- **specific conductance**
- **turbidity**
- **chloride**
- **sodium**
- **dissolved oxygen**
- **calcium**
- **magnesium**
- **alkalinity**
- **total organic carbon**
- **dissolved organic carbon**
- **soluble orthophosphate**
- **ammonia**
- **nitrate**
- **arsenic**
- **barium**
- **beryllium**
- **boron**
- **cadmium**
- **chromium**
- **copper**
- **fluoride**
- **hydrogen sulfide**
- **lead**
- **mercury**
- **nickel**
- **potassium**
- **selenium**
- **phenolic compounds**

A gas chromatograph (GC) scan should be made for chlorinated hydrocarbons, both low molecular weight solvent-like materials and higher molecular weight pesticides and PCBs; any herbicides, pesticides, and so on, used as part of maintenance of the property; plus any specific contaminants present in waste or contaminant sources that are identified by the current on-going studies of EPA and others on the characteristics of solid waste leachate. Further, for areas that are associated with
a specific source site, such as sludge lagoons and runoff water from storage areas, the list of contaminants should include any potentially hazardous materials known to have been introduced into these areas.

ANALYTICAL METHODS

In general, the analytical methods should be those procedures prescribed by EPA.4 “Standard Methods,”5 or equivalent. Care must be taken to ensure that the analytical methods used and the technician can measure each component of concern with the desired precision and accuracy. For most contaminants of concern the lower detection limit should be severalfold less than, but preferably an order of magnitude below, the critical level or standard for each particular contaminant. EPA’s “Red Book” for water quality criteria6 provides useful guides to concentrations of contaminants that may be of concern in aquatic systems.

The November 1980 Federal Register7 presents the revised EPA water quality criteria. The critical concentrations for some contaminants demonstrate the need for significantly decreasing the detection limits of the EPA’s approved analytical methods for monitoring groundwater quality. The November 1980 Federal Register lists concentrations of contaminants that are suspected to cause cancer in man when the water containing them is consumed over extended periods of time. For example, a concentration of beryllium at 3.7 x 10^3 µg/l would be expected to cause one additional cancer in a million people consuming water so contaminated, but the beryllium detection limit of the EPA procedure is 5 µg/l. This means that a municipal well located near a hazardous waste disposal site that has accepted beryllium-containing wastes could contain concentrations of beryllium in the water that are listed as nondetectable based on EPA-recommended and -approved procedures; but such water could cause an additional 1250 cancer cases in a population of a million people. The situation for beryllium is not atypical of what occurs for a number of contaminants when one compares the detection limits of the analytical methods recommended by EPA for monitoring hazardous waste disposal sites with the concentrations that EPA has determined to be potentially harmful to man through consumption of groundwaters containing the contaminants. For further discussion of the role of groundwater monitoring in situ hazardous waste disposal sites, consult Lee and Jones.8 This situation reveals the importance of being certain that hazardous waste disposal takes place in areas where the waste components are completely immobilized or detoxified and the natural geological strata do not possess any high permeability layers or lenses that would allow rapid transport of contaminants from the disposal site pits to the wells of the region.

Associated with a water quality monitoring program should be an evaluation of the reliability of the proposed sampling, handling, and analytical techniques. The investigator should never fall into the trap of the “Standard Methods” syndrome (Lee and Jones9) of assuming that a particular method, even one commonly used by others in similar types of studies, is applicable to a particular situation. The investigative approach must be used to evaluate the sampling, handling, and analytical methods on a site-specific basis. A small amount of time spent in evaluating methods can make the difference between generating considerable amounts of worthless data and developing a data base that can be used to assess the present composition of the waters being sampled as well as the changes in composition with time. Lee and Jones10,11 present discussions of problems frequently encountered in obtaining good quality analytical data. These papers, as well as the EPA quality control handbook,11 should be consulted for specific guidance on the numbers of replicate analyses, spiked samples, standard additions, and blanks that should be processed with each analytical run.

It is important that laboratory turnaround time between sample collection and data work-up be less than 2 weeks. A water quality data handling system should be established in which, as each set of data is received, it is automatically reviewed shortly after receipt to ensure that:

- It is consistent with previously collected data;
- There are no concentrations of contaminants above critical concentrations that could impair beneficial uses of the water; and
- Changes can be made in the study program, if and when needed.

Further, each year someone knowledgeable in surface and groundwater quality should prepare a report discussing what has been found from the year’s data and its potential implications for groundwater and surface water contamination.

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STUDY PROGRAM FOR DEVELOPMENT OF INFORMATION FOR USE OF OECD EUTROPHICATION MODELING IN WATER QUALITY MANAGEMENT

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ABSTRACT

The Organization for Economic Cooperation and Development (OECD) eutrophication study results provide a technical basis for assessing the impact of man's activities in a waterbody's watershed on the eutrophication-related water quality of the waterbody. In order to facilitate the use of the nutrient load - eutrophication response models developed out of this study for U.S. waterbodies, a study program has been developed to guide in the collection of necessary information in order to evaluate the applicability of the results of the US OECD eutrophication studies to a waterbody and to formulate a water quality management program for a particular lake or impoundment. This paper presents the minimum study program needed to develop US OECD nutrient load - eutrophication response couplings for a lake or impoundment's tributaries and water column. Guidance is provided on sampling frequency and location, suggested parameters to be measured, appropriate analytical methods for these measurements, and on data analysis and interpretation.
INTRODUCTION

The OECD (Organization for Economic Cooperation and Development) eutrophication modeling approach has, as its basis, statistical correlations between P load to a waterbody and various measures of planktonic algal biomass, and to related parameters to which a user may respond, such as mean summer chlorophyll (overall greenness), maximum summer chlorophyll (severity of blooms), Secchi depth (water clarity), and hypolimnetic oxygen depletion rate related to planktonic algal decomposition. These statistical correlations, as discussed by Rast and Lee (1978) and Jones and Lee (1982), are based on load and response data from about 300 waterbodies in the U.S. and abroad. The correlations have demonstrated predictive capability suitable for water quality management purposes such that the change in water quality characteristics for a waterbody that will result from a change in P load or land use can be estimated. Similarly, estimates of the amount of change in P load that will be necessary to produce given water quality characteristic values can be made using these models.

A study program designed to provide the information needed for application of the OECD eutrophication models to a waterbody must accomplish two objectives. First, it must
provide the information necessary to determine whether phosphorus is likely to be limiting maximum planktonic algal biomass during the summer growing season. Second, it should provide data which would allow for the evaluation of the applicability of the US OECD eutrophication models to the particular waterbody under investigation. Presented below is a summary of a generalized study program designed to meet these objectives. Lee et al. (1978), Jones and Lee (1982), and Rast et al. (1982) provide background information on the OECD modeling approach, US OECD load-response models, and their utility for eutrophication-related water quality evaluation and management.

It is important to emphasize that the program outlined will provide the basic information needed. If funds are available, additional samples should be collected and additional parameters of interest measured. An example of additional work that would be desirable is provided by Archibald and Lee (1981) who conducted an intensive study of Lake Ray Hubbard, a water supply impoundment near Dallas, TX.

**SAMPLING PROGRAM**

A minimum of one year's data is needed on the nutrient (nitrogen and phosphorus) loads to a waterbody and the eutrophication responses of the waterbody to these loads. Because of the year-to-year variations in the characteristics of waterbodies and in their watershed runoff caused primarily
by climatic variations, it is recommended that the study program outlined below be carried out for a three-year period.

TRIBUTARY AND OUTLET MONITORING

Sampling Frequency and Location

Preferably at weekly, but at no less than biweekly, intervals, water samples should be collected from and flow measured in each tributary of the waterbody which is expected to contribute 10% or more of the total nitrogen or phosphorus input to the waterbody. These tributaries may be preliminarily identified based on the tributary's watershed area and land use, using procedures outlined by Lee et al. (1982). These samples should be collected at a point immediately upstream of any backwater area of the waterbody and near a point suitable for tributary discharge measurements. Care should be taken to obtain representative samples of the tributary. Particular note should be made of upstream inputs which could cause concentration gradients across the width of the river. Such gradients can usually be detected by conductance and temperature profiles with depth across the river transect. If a sampling location must be selected upstream of a point source discharge to the tributary, the tributary and discharge should be sampled separately. At biweekly, but preferably weekly, intervals water samples should be collected from and flow
measured in the outlet(s) of the waterbody.

While a fixed sampling frequency is indicated in this approach, it should be realized that the optimum approach involves sampling in proportion to discharge-nutrient load patterns. As discussed by Lee (1969) and Lee and Jones (1982b), often a substantial portion of the total nutrient transport occurs during high flow periods although for some situations, such as those in which the nutrient load to the tributary is primarily from point sources, high flows serve to decrease the nutrient concentrations in the tributary with little change in total load. It is therefore important that any fixed-frequency sampling program be adjusted to include additional sampling and discharge measurements during periods of high flow such as those associated with major storm events or spring snowmelt. Attempts should be made to collect samples during both the increasing and decreasing flow periods, as indicated by the hydrograph, for that event. It should be noted that while substantial amounts of total N and total P may be transported during high flow periods, these elements may be largely associated with particulate matter; the additional load of available forms of nutrients introduced during high flow may be minimal. Procedures for determining the planktonic algal availability of tributary phosphorus have been discussed by Lee et al. (1980).
Parameters to be Measured

In order to determine nutrient load, discharge must be determined in all monitored tributaries and outlets. If possible, discharge should be measured continuously using a discharge-rated, stage level recorder. This procedure is described by the U.S. Geological Survey (USGS) (Buchanan and Somers, 1968, Chapter A7). If this is not possible, then discharge measurements should be made at the time of sampling utilizing a current velocity-cross sectional area approach as described by Buchanan and Somers (1968, Chapter A8) and Linsley et al. (1975). If discharge measurements are not made continuously, then daily discharge values should be obtained by interpolating between weekly or bi-weekly measurements. If the discharge is highly variable between measurements (such as would occur with an intense rain or snowmelt), the discharge values should be interpolated according to local precipitation or other climatological factors in accord with standard hydrological principles.

In those situations in which it is difficult to gage a tributary, it is possible to estimate the tributary discharge based on the information from a gaged tributary whose watershed has morphological and land-use characteristics similar to those of the tributary under investigation. The discharge per unit watershed area of the gaged tributary can be applied to the ungaged tributary watershed area to
estimate the tributary discharge generally with sufficient reliability for use in estimating the hydraulic residence time of and nutrient loads to the waterbody. The same approach should be used for that portion of the waterbody's watershed that lies between the gaging stations and the waterbody.

Preliminary measurements of temperature and specific conductance should be made with depth across the width of the tributary to detect stratification and concentration gradients. If the tributary at the sampling area does not show substantial temperature and/or specific conductance differences with depth or cross section (i.e., is not stratified), then generally a single sample may be collected from about mid-depth, at about mid-stream. If the tributary is vertically or horizontally stratified, it may be necessary to collect several samples which should be composited in proportion to the discharge in each component area in the tributary. A check should be made quarterly for stratification. At each sampling, weather conditions should be recorded; air temperature, cloud cover, wind direction and speed, and especially current and previous (past several days') precipitation should be noted as well as any other information that may be helpful in data interpretation.

Samples can generally be collected using a plastic bucket and rope, unless samples from specific depths are necessary. In the latter case, a Van Dorn sampler, such as that sold by Hydro Products of California, or a comparable
unit may be used. Polyethylene bottles, appropriately cleaned, are generally suitable for sample containment. Samples should be placed on ice immediately after collection and kept in the dark. A portion of the sample must be filtered through a 0.45 to 0.5 µ pore-size membrane filter (such as that manufactured by the Millipore Corporation) within a few hours after collection in preparation for the soluble ortho phosphate determination.

Water temperature should be measured at the time and location of sample collection. The tributary and outlet water samples should be analyzed for turbidity, ammonia, nitrate, total phosphorus, soluble orthophosphate, and specific conductance (corrected to 20°C). If possible, organic nitrogen analyses should also be performed on the tributary samples.

The quality of reservoir discharge water can have significant impacts on downstream water quality. If the water released from the reservoir is withdrawn from the hypolimnion and if the hypolimnion is anoxic, dissolved oxygen, total iron, total manganese, and hydrogen sulfide should be measured in the outlet samples. Specific guidance for handling and analysis of water samples is provided in a subsequent section of this manual.

The nitrogen and phosphorus loads to the waterbody should be computed by averaging the concentrations found on any two consecutive sampling dates. This average concentration should be multiplied by each of the daily estimates of
discharges for the period between the sampling dates. The daily load estimates should be summed for each month and for each year. If the study is conducted for consecutive years, then the sampling locations and frequencies should be adjusted at the end of the first year, if necessary, based on the first year's results, to yield the maximum amount of useful information for the study of the estimated nutrient loads to the waterbody with the funds available.

ATMOSPHERIC DUST-FALL AND PRECIPITATION

In order to measure the nutrient input from atmospheric sources, dust-fall - precipitation collection containers should be placed, elevated above ground, on shore in the vicinity of the dam or near the main area of water quality concern, in an area free from construction and other activities that might yield atypical dust-fall. For very long reservoirs and lakes, an additional container should be placed at the upper end of the reservoir. The dust-fall - precipitation collection container can be a 2.5 gal. (10 l) common household plastic bucket, acid washed and rinsed before use. The bucket should be placed on a small (0.5 m square) platform attached to the top of a 2 m pole. A wire ring supported from the platform by small posts or doweling should be constructed such that the ring diameter is about 6 inches (15 cm) greater than that of the bucket and such that it encircles the bucket about 4 inches (1.2 cm) above
the top of the bucket. The purpose of this wire ring is to provide a roost for birds to prevent them from defecating in the bucket.

The collection bucket(s) should be left out for one month to collect both precipitation and dry fallout, before it is replaced with another bucket. If there is no water or less than 500 ml of water in the bucket at the end of the collection period, the volume should be brought to 500 ml with deionized water. If there are 500 to 1000 ml of water in the bucket, the volume should be adjusted to 1 liter. Adjusted sample volume should be recorded. If the volume at collection is greater than 1 liter, the volume should be measured and recorded but no dilution made. Following sample volume adjustment if necessary, the pH should be adjusted to 1 ± 0.5 with HCl. The acidified sample should be allowed to stand in the collection bucket overnight. It should then be filtered through a 0.45 to 0.5 µ pore-size membrane filter which has been pre-rinsed as described in a subsequent section. Acidified samples should be analyzed for nitrate, ammonia, soluble ortho P, and total P concentrations.

LAKE OR IMPOUNDMENT MONITORING

Sampling Location

For many waterbodies, a single sampling station provides adequate data for a nutrient load - eutrophication
response study; however, for some waterbodies, especially elongate waterbodies, several sampling sites are needed in order to properly define nutrient load–eutrophication response relationships. In order to determine the appropriate sampling location(s), the specific area of water quality concern should be identified (i.e., main body or an arm of the waterbody), the hydrological and morphological characteristics (such as hydraulic residence time and shape, etc.) of the waterbody should be examined, and preliminary measurements should be made of specific conductance to assess mixing properties. If the waterbody has no significant arms and appears to be fairly well mixed horizontally, based on specific conductance measurements, one sampling site at the deepest part of the waterbody is generally sufficient for the purposes of these studies. If, however, as discussed by Archibald and Lee (1981), the waterbody has arms from which the flow to the main body is restricted, the arms should be considered as separate units, each having its own load-response relationship and its own load to the main body; these should be sampled separately. Such arms, as well as upstream waterbodies, tend to act as nutrient traps in which appreciable amounts of algal-available nitrogen and especially phosphorus may be removed from solution and incorporated into the sediments. This phenomenon should be suspected any time the hydraulic residence time (volume : inflow) of the upstream waterbody or arm during the summer growing season is greater than about two weeks. During the
summer, two weeks are adequate for substantial algal growth to occur and result in the removal of available phosphorus from the water column.

For elongate waterbodies, if no substantial constrictions exist, the hydraulic residence time of the upper quarter as well as of the overall waterbody should be computed assuming plug flow of the inflow tributary water through the waterbody, that is, residence time should be computed by dividing the volume of the waterbody, or waterbody segment, by the inflow. Further, a set of preliminary samples should be collected at four locations along the length of the waterbody for determination of specific conductance, chlorophyll, total phosphorus, soluble orthophosphate, ammonia, and nitrate. Based on the experience of the authors, consideration should be given to establishing more than one sampling site in a waterbody if a) the hydraulic residence time of the upper quarter of the waterbody is two weeks or more, or b) the specific conductance varies between any two segments by more than 40 to 60 μmhos/cm @ 20° C, or c) if the chlorophyll, phosphorus, or nitrogen concentrations along the length of the waterbody vary by more than a factor of 10. It is important to note that these values should not be taken as absolute; each waterbody's characteristics should be critically evaluated and decisions made based on those characteristics using the above ranges as general guides. Data collected during the summer growing
season should be examined promptly to determine if the differences in concentrations are maintained. If the summer average concentrations of all of these parameters consistently vary between stations by a factor of less than about 10 then, based on the authors' experience, consideration should be given to eliminating some of the sampling sites.

**Sampling Depths**

In order to determine from which depths water samples should be collected, it must be determined if the waterbody is density stratified due to temperature or salts at the sampling site(s). To do so, temperature, dissolved oxygen (D.O.), and specific conductance should be measured at each sampling location at 0.5 m below the surface, at mid-depth, and a - 0.5 m off the bottom. If the surface water temperature is 10° C or less, the water column should be considered stratified if the average temperature decrease with depth is about 1 C°/m. If the surface water temperature is about 20° C, the water column should be considered stratified if the average temperature decrease with depth is about 0.5 C°/m. It is important to note that it is not the temperature change per se that determines stratification, but rather the density difference caused by the temperature difference. At higher water temperatures, a fraction of a centigrade degree change in temperature will have the same impedance to the mixing of surface and bottom waters as a 1 to 2 C°
change at lower temperatures.

If the waterbody is not thermally stratified at the sampling site, water samples should be collected from 0.5 m below the surface, mid-depth, and 0.5 m off the bottom. If the waterbody is thermally stratified, temperature should be measured every 0.5 m through that portion of the water column in which the maximum temperature difference exists in order to define the location of the thermocline. The thermocline is defined as the depth of the point of inflection on the temperature vs. depth curve (i.e., when the slope of the curve changes sign). Under stratified conditions, water samples should be collected from and D.O. measured at the following depths: 0.5 m below surface, 1 m above the thermocline, 1 m below the thermocline, 0.5 m off bottom, halfway between the thermocline and the surface, and halfway between the thermocline and bottom. A similar sampling approach should be used when density stratification due to salts occurs, using changes in specific conductance as guidelines.

During certain times of the year, the bulk density of tributary waters to some lakes and reservoirs is such that the input water sinks below the surface water of the waterbody, forming a layer or density current rather than mixing with the surface waters. Such density currents may be detected by measuring temperature, specific conductance and/or turbidity with depth in the waterbody. If this phenomenon is encountered at the in-lake sampling stations, i.e., a
layer is detected which shows atypical concentrations of one or more of these parameters which is not due to measurement problems, additional samples should be collected to define the areal and vertical extent of the density current and its composition.

**Frequency of Sampling**

While a one year sampling program may be adequate to define general nutrient load - eutrophication response relationships for a waterbody, it is highly desirable to conduct the sampling program throughout a three-year period in order to take into account year-to-year variability in waterbody characteristics. As a minimum during the winter-spring, samples should be collected at each sampling site in the waterbody on about January 15, February 15, March 15, and April 15. Samples should be collected every two weeks during May, June, July, August, and September, although it would be desirable to have weekly samples during the summer. Samples should also be collected on about October 1, November 1, and December 1. If the waterbody has a marked spring algal bloom, samples should be collected at biweekly intervals during this period to define the bloom characteristics.

The Van Dorn water sampler (with messenger) has been found to be suitable for collecting in-lake water samples. Some investigators have found it desirable to use a 6-liter capacity Van Dorn in order to collect a sample of sufficient
volume for analysis. This is especially important for waterbodies having low chlorophyll concentrations. Other similar equipment which is equally suitable for sample collection is also available. Polyethylene bottles, appropriately washed, are suitable for sample containment.

All water samples should be put on ice immediately after collection and kept in the dark. A portion of each sample must be filtered within a few hours of collection in preparation for soluble orthophosphate determination. The procedure that must be followed for filtering is described in a subsequent section of this manual (under the phosphorus procedure). Sample collection and handling are also discussed in a subsequent section.

Parameters to be Measured

In Situ Measurements

At the time of sample collection, dissolved oxygen and temperature should be measured in the water column at the same depths from which water samples are taken. It is recommended that the YSI (Yellow Springs Instrument Co., Yellow Springs, Ohio) Model 54 dissolved oxygen meter and probe be used to make these measurements. There are a number of seemingly comparable instruments available to make these measurements, however, many of them have been found to be unreliable; the YSI Model 54 has proved to be highly reliable for this purpose. The probe cable purchased
should be of sufficient length so as to reach the bottom of the deepest waterbody being studied.

At each sampling, weather conditions should be recorded; air temperature, cloud cover, wind direction and speed, and current and previous (past several days') precipitation should be noted, as well as any other information that might help in data interpretation. For waterbodies in which the water depth varies substantially over the annual cycle, surface water elevation records should be obtained.

Secchi depth should be determined at each sampling station at the time of sampling. The Secchi depth is determined using a Secchi disc, a 20 cm diameter disc having alternating black and white quadrants, suspended from a graduated line. The disc is lowered into the water until no longer clearly visible; this depth is recorded. The disc is then lowered an additional meter into the water and slowly raised until it is just visible; this depth is also recorded. The average of these two depths is the Secchi depth value. The cable from which the Secchi disc is suspended should be marked at half meter intervals, with the first meter closest to the disc being marked every 10 cm for ease and desired accuracy of reading. Secchi discs can be purchased from scientific supply companies or can be readily constructed. It is important to note that all-white discs or discs of different diameters can yield Secchi depth values different from those of a standard 20 cm, black/white disc; for consistency and comparability, therefore, the recommended
disc should be used. If a different type of disc is used, its characteristics should be reported.

Since light penetration into water is a logarithmic function of depth, in order to average Secchi depth values, the arithmetic mean of the logarithms of the Secchi depths should be determined. The antilog of that mean value is the average Secchi depth.

An estimate of the areal extent of aquatic macrophyte and attached algae cover in the waterbody should be made at each sampling. Any information available on fish yield from the waterbody should also be collected and reported. This latter type of information is often available from local or state fisheries personnel.

Laboratory Determinations

The following parameters should be measured on each water sample as soon as possible after collection: total P, soluble ortho P (on filtered sample), ammonia, nitrate, chlorophyll (within 24 hours after collection), specific conductance, and pH. It is also desirable to measure organic N in the samples. In the samples collected at 0.5 m beneath the surface, the dominant types of phytoplankton should be identified to genus. Once during the winter, once during the summer, and once during the spring bloom (if one occurs), the alkalinity and soluble reactive silica should be determined in all in-lake samples. If the
waterbody of interest is a reservoir for which a water supply intake or the reservoir outlet is located below the thermocline, total iron, total manganese, and hydrogen sulfide should be measured in all in-lake samples collected when the hypolimnion is anoxic.

The specific analytical procedures recommended for use in connection with this study have been largely derived from the Standard Methods for Examination of Water and Wastewater, 15th Edition ("Standard Methods") (APHA et al., 1981). These have been found to meet the needs of this type of study. Other procedures such as some found in US EPA (1979b) will also likely be suitable for this purpose, but it is important that any other procedure that may be considered for use, instead of one of the following, be carefully evaluated to be certain that it provides sensitivity and reliability for the water being examined at least equal to that of the recommended method. It is also important that an analyst not casually use other methods presented in APHA et al. (1981), instead of those recommended herein. Many of them are not reliable for determination of particular parameters under the conditions that exist in the type of natural water systems likely to be encountered in a study of this type and should, like any method, be carefully evaluated prior to use. All investigators should become familiar with the introductory sections of APHA et al. (1981), as well as with the sections pertinent to the study, which are listed below. (Section and page number
notations refer to sections and pages in APHA et al. (1981).

Collection and Preservation of Samples. Section 105.
(Pages 35-41). Presented in Standard Methods Section 105
is a discussion of a variety of sample preservation tech­
niques. For the purpose of nutrient load - eutrophication
response studies, it is recommended that the procedure
outlined below be followed. Water samples should be held
in polyethylene or other suitable bottles which should have
been washed with detergent, rinsed thoroughly with tap
water, rinsed with dilute (10 to 20%) HCl, and rinsed five
times with deionized water. Samples should be put on ice
as they are collected and kept in the dark. A portion of
the sample must be filtered within a few hours of collection
through a 0.45 to 0.5 μ pore-size membrane filter which has
been pre-rinsed (as described in APHA et al. (1981) Section
424A). The filtered sample for soluble orthophosphate de­
termination should be kept on ice and in the dark until re­
turned to the laboratory. In the laboratory, all samples
should be stored in the dark at a temperature just above
freezing. Chlorophyll determination on the sample must be
initiated within 24 hours of sample collection. Each sam­
ple must be mixed well before aliquots are withdrawn for
any analysis.

If it is necessary for samples (other than chlorophyll)
to be stored for a period of time longer than approximately
one week before analysis, the samples should be preserved
with suitable reagents for the parameters being determined.
All preservation techniques considered for use must be evaluated for their ability to maintain sample integrity for the parameters being measured. There are some who believe that samples for chlorophyll analysis can be preserved by freezing. Before this is done, a study should be conducted to assess the suitability of this technique for the numbers and types of algae, and other characteristics of the water in the particular waterbody.

**Conductivity. Section 205. (Pages 70-73).** A general discussion of conductivity measurements is presented in APHA et al. (1981) Section 205. The YSI Model 33 S-C-T meter has been found to be suitable for both the field and laboratory measurements of specific conductance. All specific conductance measurements should be corrected to 20° C as outlined in Section 205 if the instrument used does not automatically make this correction.

**Temperature. Section 212. (Pages 124-125).** Temperature should be measured in accord with the discussion in Standard Methods Section 212.

**Turbidity. Section 214. (Pages 131-138).** Turbidity should be measured following the Standard Methods Section 214A Nephelometric Method. The Hach 2100A Turbidimeter has been found to be especially suitable for making these measurements.

**Alkalinity. Section 403. (Pages 253-257).** Alkalinity should be determined by titration with a standard acid using a colorimetric indicator as described in APHA et al. (1981)
Section 403.

Nitrogen. Section 416. (Pages 350-351). The introductory section on Nitrogen (Section 416) should be reviewed for background information.

Nitrogen (Ammonia). Section 417. (Pages 351-367). The recommended procedure for determination of ammonia is the Orion Specific Ion Electrode Method. The procedure outlined in the manual provided by Orion Research Company (Cambridge, MA) for the ammonia electrode should be followed; guidance on the use of this method is presented in Standard Methods Section 417E, Pages 362-363. The duration of measurement should be of sufficient length to allow detection of ammonia at 0.02 mg N/l. For these types of studies there is no need to achieve greater sensitivity than this by extending the duration of measurement (equilibration time). It is desirable, because of the sometimes relatively short lifetime of the ammonia electrodes, to initially purchase two electrodes. When one electrode no longer functions, the extra one can be used; meanwhile, another should be ordered.

A suitable substitute for the Specific Ion Electrode Method of ammonia measurement is the Nesslerization Method following distillation as described in APHA et al. (1981) Section 417B. The direct nesslerization procedure is generally unreliable for many natural waters and should not be used for these studies without careful evaluation of its suitability for the waters being investigated. It
has been found by the authors that the method for ammonia analysis described by Solorzano (1969) provides results essentially identical to those obtained using the Orion electrode method and nesslerization following distillation.

**Nitrogen (Nitrate). Section 418. (Pages 367-380).**

It is recommended that nitrate be determined using the Cadmium Reduction Method as described in APHA et al. (1981) Section 418C. It is necessary that the laboratory doing the analyses be able to reliably measure nitrate at 0.02 mg N/l.

**Nitrogen (Organic). Section 420. (Pages 383-388).**

Organic nitrogen measurements are not mandatory but are highly desirable for this type of study. If the analysis is made, the procedure outlined in APHA et al. (1981) Section 420A and B should be followed.

**Oxygen (Dissolved). Section 421. (Pages 388-399).**

When the Winkler (iodometric) procedure is used for dissolved oxygen measurement, the Azide Modification procedure (Section 421B) should be followed. It is recommended that the field determination of dissolved oxygen be made with the YSI Model 54 dissolved oxygen meter or equivalent. The Membrane Electrode Method is described in APHA et al. (1981) Section 421F.

**pH. Section 423. (Pages 402-409).** It is recommended that the glass electrode method be used for pH determination. This procedure is outlined in APHA et al. (1981) Section 423. The electrode system should be calibrated,
generally using buffers of pH 6 and 10, unless the pH of the water being analyzed is out of that range; in that case, buffers should be chosen to cover the range expected. Commercially prepared buffer solutions are suitable for use in calibration.

Since pH is a logarithmic function of the hydrogen ion activity, in order to average pH values, the arithmetic means of the antilogs of the pH values must be determined; the log of that mean is the average pH.

**Phosphate. Section 424. (Pages 409-426).** For soluble orthophosphate determination, the preliminary filtration step described in APHA et al. (1981) Section 424A, should be followed. Within a few hours after collection, the sample should be filtered through a 0.45 to 0.5 μ pore-size membrane filter which has been rinsed prior to filtration with dilute HCl, then deionized water, or soaked in deionized water as described in Section 424A of Standard Methods (page 412). The Ascorbic Acid Method (Standard Methods Section 424F) should be used to determine the soluble ortho P content in the filtered sample. It is important that the analyst be able to reliably measure soluble ortho P at 2 to 3 μg P/l levels. This will require the use of a spectrophotometer cell path length of at least 5 cm but preferably 10 cm.

For total phosphorus, the sample must be digested as outlined in APHA et al. (1981) Section 424C. Procedure III - Persulfate Digestion Method presented in Section 424C
is generally suitable for waters having fairly low turbidity, such as would typically be encountered in this type of study. For highly turbid samples, it may be necessary to add additional persulfate to effect complete digestion of the sample. Digestion should be followed by the Ascorbic Acid Method, (Section 424F) for measurement of orthophosphate. As outlined in Section 424C, the standards should also be processed through the digestion step.

Silica. Section 425. (Pages 426-436). Samples collected for silica analysis must be filtered through a 0.45 to 0.5 μ pore-size membrane filter within a few hours of collection. The Heteropoly Blue Method outlined in APHA et al. (1981) Section 425D, should be used on the filtered sample.

Plankton. Section 1002. (Pages 931-950). Samples for plankton examination should be collected using a Van Dorn water sampler as described in APHA et al. (1981) Section 1002B, or equivalent. The sample collected for phytoplankton identification should be preserved using Lugol's solution as described in APHA et al. (1981) Section 1002B. While the sedimentation concentration method is generally preferred, the membrane filtration method of concentration described in APHA et al. (1981) Section 1002C (page 939) is adequate for the purpose of this study; the concentration technique used should be specified when reporting the data. The concentrated sample should be examined in a Sedgwick-Rafter counting cell or equivalent (Section 1002F).
using 200X magnification; approximately 10 fields, i.e., the total area visible, should be examined. The 5 to 10 most prevalent genera should be identified (to genus level only). There is no need in this type of study for detailed classification or enumeration of all types of phytoplankton present.

Section 1007 of APHA et al. (1981) presents a general discussion of identification of aquatic organisms including phytoplankton. Also provided is a key for the identification of freshwater algae along with illustrations (Section 1007D). A reference section (1007G) provides references to other work useful for identification of algae.

Since many water utilities routinely count and identify algae and have many years' record of this type of information, it may be desirable to initiate a program of measuring chlorophyll and pheophytin in samples on which detailed algal counts are made by the water utility. After a year or so of weekly data (or if less frequently sampled, longer periods of time) being accumulated, it may be possible to develop statistical correlations between the planktonic algal chlorophyll concentrations and the numbers and types of algae present. While correlations of this type are often highly scattered, they are frequently of sufficient reliability to enable estimates to be made of the past planktonic algal chlorophyll concentrations in the waterbody based on previously collected algal count and identification data. This historical information is often of assistance
in determining the impact of man's past activities on the waterbody characteristics and in predicting future impacts. For additional information on chlorophyll measurements and the use of these measurements as a water supply water quality parameter, consult Lee and Jones (1982a).

Chlorophyll. Section 1002G. (Pages 950-954). The spectrophotometric or the fluorometric procedure outlined in APHA et al. (1981) Section 1002G should be followed for chlorophyll and pheophytin determination, the latter method being more suitable for low levels of chlorophyll; only total chlorophyll a and pheophytin a need be determined. Total chlorophyll a should be calculated using the Trichromatic Method (page 950); pheophytin should be calculated as described in subsection 3, page 953. "Corrected" chlorophyll is determined by subtracting the pheophytin from the total chlorophyll. Both total and corrected chlorophyll concentrations should be reported in addition to pheophytin. Samples collected for chlorophyll determination must be kept on ice or refrigerated at just above freezing and in the dark until analysis. Analysis must be initiated within 24 hours after sample collection. Additional details on the determinations of chlorophyll are provided by Lee and Jones (1982a).

Hydrogen Sulfide. Section 427. (Pages 442-450). The Methylene Blue Method (Section 427C) should be suitable for measurement of hydrogen sulfide in this study program. The Orion specific ion electrode method can also be used.
Manganese. Section 319. (Pages 213-217). A procedure such as that outlined in Standard Methods Section 319B, the Persulfate Method, should be used for total manganese determination.

Iron. Section 315. (Pages 199-206). Total iron should be determined by the Phenanthroline Method (Section 315B) or equivalent.

Other Parameters

It is advisable for the investigator to periodically (quarterly) collect samples for measurement of toxicants such as heavy metals, pesticides, and potentially hazardous organics which may be discharged to tributaries of the waterbody from municipal, industrial, or other sources. While such parameters may not significantly affect the growth of algae or other aquatic plants, they can impact those beneficial uses for which eutrophication is of major concern, such as fisheries and water supply and, hence, may impact management decisions. The additional cost of these analyses would normally be only a small part of the total program costs. An application of this study program, which included heavy metals and other toxic parameters, to a proposed domestic water supply reservoir was developed by Lee and Jones (1991).

Laboratory Analytical Quality Control. A key component of any water quality study involving chemical or biological
analysis of samples is the quality assurance program followed in the study. The U.S. Environmental Protection Agency has devoted considerable effort to developing quality assurance programs for data generated in studies of this type. The guidance presented below is based largely on the work of the US EPA and the authors.

APHA et al. (1981) Section 104 (pages 18-35), "Precision, Accuracy and Correctness of Analyses," as well as the US EPA Handbook for Analytical Quality Control in Water and Wastewater Laboratories (US EPA, 1979a) Chapters 6 and 7, provide detailed discussions of approaches for determining the precision and accuracy of analytical determinations. Further, they provide guidance on routine quality control procedures that should be followed to ensure consistent, high-quality data. It is recommended in accord with Booth (1979), that the following quality control procedures be routinely followed for all laboratory determinations.

a) For each set of samples processed, duplicate determinations should be performed on 15% of the samples. These samples should be selected at random.

b) For each set of samples processed, "spikes" should be prepared for 15% of the samples (also chosen at random). This means that, in addition to running the water sample as usual, a separate aliquot of
the sample is prepared to which a known amount of
the material being measured is added. This addi-
tion ("spike") should approximately double the con-
centration of the parameter being determined in
the sample.

c) For those determinations in which a standard curve
is used, the standard curve must be verified for
each set of samples processed. As a minimum, a
deionized water blank and three standard solutions
(low, mid-range, and high points on the curve)
should be run with each set of samples.

d) When using an instrument such as a spectrophoto-
meter, the operator should periodically spot-check
the calibration curve by measuring the instrument's
response to a sample of known concentration in the
middle of the concentration range being considered.
This standard should be run after approximately
each 10% of the samples are run.

e) In situations where more than one laboratory is
conducting analyses for a study, on a quarterly
basis a central laboratory should prepare standard
known solutions of each parameter being determined,
and distribute them to the laboratories involved,
without indicating the nature of the samples. The
results of these analyses should be reviewed to
determine if the error among them is acceptable.
If a contract laboratory is performing analyses on behalf of a contractor, the contractor should set up a quality assurance program in addition to that one being conducted within the laboratory. The contractor should, on a roughly quarterly basis, submit to the laboratory water samples with known amounts of the materials being determined, replicate water samples, and standard samples which are completely synthetic and contain accurately known amounts of selected contaminants. These samples should be submitted in such a way that they are in no way distinguishable from routine samples. If a laboratory does not conform to required analytical precision and accuracy, their services should not be retained.

A key part of the reporting of the data in connection with a study of this type is the presentation of the data obtained in the quality assurance program. The results of the quality assurance program should be evaluated in light of the guidance given by US EPA (1979a) and the intended use of the data (i.e., the precision and accuracy required). Some laboratories have found that quality control charts such as those presented in *Standard Methods* are useful for maintenance of adequate quality control. The data reports and final report should present the quality assurance data and should include a statement concerning the reproducibility of the analytical procedure, the ability to recover spikes, etc.
Morphometric and Hydrologic Characteristics

To determine a waterbody's mean depth, divide the volume by the surface area. The hydraulic residence time can be determined by dividing the waterbody volume by the inflow or outflow rate. These two procedures, i.e., using inflow rate vs. outflow rate, may yield substantially different hydraulic residence times; both values should be reported. For waterbodies in which the volume fluctuates greatly over an annual cycle, the values chosen to compute the mean depth and hydraulic residence time should be chosen with great care. Jones and Lee (1982) provide guidance on how these selections should be made.

Data Manipulation

In order to compute average concentrations of nitrogen, phosphorus, chlorophyll, and other characteristics of the waterbody, it is necessary to interpolate between the sampling points in order not to bias the mean by the sampling frequency used. All data should be converted to a weekly basis; two consecutive biweekly data points should be averaged, thus providing an estimate of the concentration of the parameter for the week in between, when no samples were collected. If the sampling interval is greater than two weeks, the two consecutive sample data should be averaged; the average values should be assumed to be applicable to the weeks in between sampling dates. This two-point moving
average should be performed over the sampling period to provide weekly data.

To assess overall eutrophication response of the waterbody as measured by phytoplankton biomass, the annual mean and summer mean chlorophyll concentrations should be determined. In the manner described above, weekly values of chlorophyll concentration should be determined and then averaged. During periods of stratification the epilimnetic values should be averaged, and during isothermal periods the average should be calculated using data from all depths. The average phosphorus concentrations found in the waterbody, which include both epilimnetic and hypolimnetic values during the summer, should be compared to the predicted average phosphorus using the procedure developed by Vollenweider (1976) and described for application by Lee et al. (1981), based on the average P input concentration and the hydraulic residence time.

The weekly or biweekly tributary flow measurements should be plotted as a function of time, and daily flow values estimated. As discussed previously, these daily averages should be used to determine contaminant load and overall water input. While more sophisticated methods of averaging can be used, the simple averaging described above should be sufficient to meet the needs of this type of study.
DATA REPORTING

All data obtained in the study should be tabulated for inclusion in an appendix to the overall final report. Included should be the quality assurance data on replicate samples, spiked samples, etc., with an indication of the magnitude of the spike, amount recovered, etc.

INTERPRETATION OF DATA

Lee and Jones (1979) have described the procedure that should be used for initial evaluation-interpretation of data of the type that will be obtained in a nutrient load-response study of the sort described in this manual. It is important that data analysis be conducted in accord with procedures outlined by Lee and Jones (1979). Data should be reviewed as they are developed; an investigator should not wait until all data are collected before beginning to review them.

The interpretation of the data in terms of nutrient load - eutrophication response and water quality management should be made through the OECD eutrophication models. Use of these models has been discussed by Rast and Lee (1978), Jones and Lee (1982), Lee et al. (1978), Horstman et al. (1980), and Archibald and Lee (1981).
RELATIONSHIPS BETWEEN PLANKTONIC ALGAL
CHLOROPHYLL CONCENTRATION AND WATER SUPPLY
AND OTHER WATER QUALITY CHARACTERISTICS

The OECD eutrophication modeling approach utilizes average planktonic algal chlorophyll concentration as the primary eutrophication response parameter of a waterbody. This parameter is indicative of a wide variety of water utility problems such as algal taste and odor, activated carbon use, algal-related shortened filter runs, increased chlorine demand and possibly, for some waterbodies, increased concentrations of trihalomethane precursors. It is also indicative of potentially adverse impact to recreation-related beneficial uses of the water, such as boating, swimming, and fishing.

The relationships between raw water quality problems or problem-causing organisms and planktonic algal chlorophyll concentrations are not well known at this time primarily as a result of the fact that few water utilities measure planktonic algal chlorophyll concentration in their water. The adoption of this study plan, or as a minimum, the routine measurement of planktonic algal chlorophyll concentration, should enable a water utility to develop correlations between planktonic algal chlorophyll concentration and the raw water quality characteristics for their water supply(ies). Since it is possible, through the use of the OECD eutrophication modeling approach, to relate
planktonic algal chlorophyll concentration to a waterbody's phosphorus load, and since many of the water quality characteristics of water supplies can be related to increased cost of treatment, water utilities which adopt this program will be able to relate changes in P load to their raw water supply to changes in costs of preparing a finished water.

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