Study Program for Development of Information for Use of Vollenweider-OECD Eutrophication Modeling in Water Quality Management for Lakes and Reservoirs

G. Fred Lee, Ph.D., P.E., President
and
R. Anne Jones, Ph.D., Vice-President
G. Fred Lee & Associates
El Macero, California

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 that study for US waterbodies, a study program outline has been developed to guide the collection of information needed to evaluate the applicability of the results of the US OECD eutrophication studies to a waterbody that can be used as a basis for formulation of 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 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 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), Jones and Lee (1982a, 1986), and Lee and Jones (1988, 1991e) are based on load and response data from about 500 waterbodies in the US 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 (Rast *et al.*, 1983). 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. It should provide the information necessary to determine whether the phosphorus loads to the waterbody are likely to be correlated with the average planktonic algal biomass during

the summer growing season. 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), Lee and Jones (1988, 1991e), Jones and Lee (1982a, 1986), and Rast *et al.* (1983) 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, however, 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, Texas.

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 climate 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 Rast and Lee (1983). 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 tributary. Such gradients can usually be detected by electrical 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), 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 those events. 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 US 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 biweekly 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. As a guideline, temperature differences of more than 3 to 5^{o}C or specific conductance differences of more than about 50 µmhos/cm @ 20^{o}C at a transect or with depth at a single location should signal the possibility of a water's being stratified.

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 may be used. Polyethylene bottles, appropriately cleaned as discussed subsequently, 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 pre-rinsed 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 orthophosphate 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 $20^{o}C$). If possible, organic nitrogen analyses should also be performed on the tributary samples.

The characteristics 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 (10 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 with deionized water. Adjustments to the 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 or those with a number of major arms, 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 in 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 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 from the center of the waterbody at 0.5-m and mid-depths, and 0.5 m off bottom, 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, b) the specific conductance varies between any two segments by more than 40 to 60 μmhos/cm @ 20^{o}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 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.

If the waterbody is segmented along its length, or if it has arm or bay areas, the "outlets" of each of these areas should be sampled at at least monthly intervals to define the concentrations of nutrients in the surface, mid-depth, and bottom waters. These data can then be used with the tributary flows to the segments, to compute the nutrient load from the "upper" waterbody segment to the "lower" segment. This will provide more appropriate nutrient loading estimates for lower portions of waterbodies, frequently the main bodies of reservoirs near the dams, than could be obtained using tributary inputs to any waterbody as a whole.

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 (DO), and specific conductance should be measured at each sampling location at 0.5 m below the surface, at mid-depth, and at 0.5 m off the bottom. If the surface water temperature is 10^{o}C or less, the water column should be considered stratified if the average temperature decrease with depth is about 1 ^{o}C/m. If the surface water temperature is about 20^{o}C, the water column should be considered stratified if the average temperature decrease with depth is about 0.5^{o}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 ^{o}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 DO 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. In some waterbodies, stratification can be detected by changes in dissolved oxygen concentrations with depth.

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 and Duration 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. In temperate Northern Hemisphere climates, 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. In the Southern Hemisphere, the sampling dates should be adjusted for the differences in seasons.

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 subsequent sections.

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 or the Hydrolab (Austin, Texas) submersible probe or other similar equipment 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 and the Hydrolab equipment have been 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 the black and white quadrants are no longer clearly distinguishable from one another; this depth is recorded. The disc is then lowered an additional meter into the water and slowly raised until the quadrants are just distinguishable; 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, within about 24 hours of collection: total P, soluble ortho P (on filtered sample), ammonia, nitrate, specific conductance, and pH. It is also desirable to measure organic N in the samples. In the samples collected in epilimnetic waters, and in samples collected in surface and mid-depth waters of unstratified waterbodies, chlorophyll and pheophytin should be measured within 24 hours of sample collection. In the samples collected at 0.5 m beneath the surface, the dominant types of phytoplankton should be identified to genus level. 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 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 the Examination of Water and Wastewater, 17th Edition, ("Standard Methods") (APHA *et al.*, 1989). These have been found to meet the needs of this type of study. Other procedures, such as some found in the US EPA (1983) methods manual, will also likely be suitable for this purpose, but it is important that any procedure that may be considered for use other than 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. Since these methods are periodically updated, the analyst should use the most recent version of the same method as those specified below. It is also important that an analyst not casually use other methods presented in APHA *et al.* (1989) or US EPA (1983) 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.* (1989), 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.* (1989).]

Collection and Preservation of Samples. Section 1060. (Pages 1-30 - 1-40). Presented in Standard Methods Section 1060 is a discussion of a variety of sample preservation techniques. For the purpose of nutrient load-eutrophication response studies, it is recommended that the procedure outline 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.* (1989) Section 4500-P B Sample Preparation]. The filtered sample for soluble orthophosphate determination should be kept on ice and in the dark until returned 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 sample 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 2510. A general discussion of conductivity measurements is presented in APHA *et al.* (1989) Section 2510. The YSI Model 33 S-C-T meter or Hydrolab probe has been found to be suitable for field measurements and the YSI meter for laboratory measurements of specific conductance. All specific conductance measurements should be made at 20^{o}C or 25^{o}C as outlined in Section 2510. If measurements are made at another temperature and if the instrument used does not automatically make this correction, experimentally determine the correction factor for the water by measuring the conductance of the water as a function of temperature. This correction is typically on the order of 2 to 2.5% per centigrade degree. The temperature to which the measurements have been corrected should be reported.

Temperature. Section 2550. Temperature should be measured in accord with the discussion in Standard Methods Section 2550.

Turbidity. Section 2130 B. Turbidity should be measured following the Standard Methods Section 2130 B Nephelometric method. The Hach 2100A Turbidimeter has been found to be especially suitable for making these measurements.

Alkalinity. Section 2320. Alkalinity should be determined by titration with a standard acid using a colorimetric indicator as described in APHA *et al.* (1989) Section 2320.

Nitrogen. Section 4500-N. The introductory section on Nitrogen (Section 4500-N) should be reviewed for background information.

Nitrogen (Ammonia). Section 4500-NH_3. 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 4500-NH_3 F. 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.* (1989) Section 4500-NH_3 C. 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 4500-NO_3. It is recommended that nitrate-plus-nitrite be determined using the Cadmium Reduction Method as described in APHA *et al.* (1989) Section 4500-NO_3 E. These results must be labeled as nitrate-plus-nitrite. It is necessary that the laboratory doing the analyses be able to reliably measure nitrate at 0.015 mg N/L.

Nitrogen (Organic). Section 4500-N_{org}. 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.* (1989) Section 4500-N_{org} B or C should be followed, using the Nesslerization or electrode option for final ammonia measurement. As these methods determine "Kjeldahl" nitrogen, the ammonia concentration must be subtracted from this value to yield the organic nitrogen concentration.

Oxygen (Dissolved). Section 4500-O. When the Winkler (iodometric) procedure is used for dissolved oxygen measurement, the Azide Modification procedure (Section 4500-O C) should be followed. It is recommended that the field determination of dissolved oxygen be made with the YSI Model 54 dissolved oxygen meter, Hydrolab probe, or equivalent. The Membrane Electrode Method is described in APHA *et al.* (1989) Section 4500-O G.

pH. Section 4500-H^+. It is recommended that the glass electrode method be used for pH determination. This procedure is outlined in APHA *et al.* (1989) Section 4500-H^+. The electrode system should be calibrated, generally using buffers of pH 7 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.

Phosphorus. Section 4500-P. For soluble orthophosphate determination, the preliminary filtration step described in APHA *et al.* (1989) Section 4500-P B 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 4500-P B of Standard Methods. The Ascorbic Acid Method (Standard Methods Section 4500-P E) should be used to determine the soluble ortho P content of the filtered sample. It is important that the analyst be able to reliably measure soluble ortho P at the 2-to-3-µg P/L level. 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.* (1989) Section 4500-P B. Procedure 5 - Persulfate Digestion Method presented in Section 4500-P 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 4500-P E), for measurement of orthophosphate. As outlined in Section 4500-P E, the standards should also be processed through the digestion step.

Silica. Section 4500-Si. 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.* (1989) Section 4500-Si E should be used on the filtered sample.

Plankton. Section 10200. Samples for plankton examination should be collected using a Van Dorn water sampler as described in APHA *et al.* (1989) Section 10200, or equivalent. The sample collected for phytoplankton identification should be preserved using Lugol's solution as described in APHA *et al.* (1989) Section 10200. While the sedimentation concentration method is generally preferred, the membrane filtration method of concentration described in APHA *et al.* (1989) Section 10200 C is adequate for the purpose of this type of 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 10200 F) 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 10900 of APHA *et al.* (1989) 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. A reference section (10900 G) provides references to other work useful for identification of algae.

Since many water utilities routinely count and identify algae and have many years' records 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 accumulating weekly data (or if samples are collected less frequently, longer periods of time), 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 Jones and Lee (1982b).

Chlorophyll, Section 10200 H. Spectrophotometric or the fluorometric procedure outlined in APHA *et al.* (1989) Section 10200 H 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 10200 H 2; pheophytin should be calculated as described in the same section. "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 Jones and Lee (1982b).

Hydrogen Sulfide. Section 4500-S^{2-}. The Methylene Blue Method (Section 4500-S^{2-} D) should be suitable for measurement of hydrogen sulfide in this type of study program. The Orion Specific Ion Electrode Method can also be used.

Manganese. Section 3500-Mn. A procedure such as that outlined in Standard Methods Section 3500-Mn, the Persulfate Method, should be used for total manganese determination.

Iron. Section 3500-Fe. Total iron should be determined by the Phenanthroline Method (Section 3500-Fe D) 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 made by Lee and Jones (1981).

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.* (1989) Section 1020, "Quality Assurance," as well as the US EPA Handbook for Analytical Quality Control in Water and Wastewater Laboratories (US EPA, 1979) Chapters 6 and 7, (use latest edition) 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 through each analysis, "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 of a volume half that normally used for analysis is combined with an equal volume of a solution containing the chemical being analyzed at a known concentration approximately the level expected in the sample. Thus the concentration of the parameter in this "spiked" sample should be approximately equal to, or at least be close to the concentration in the original 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 spectrophotometer, 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 or in-house 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 and the cause of the problems cannot be identified and corrected, another laboratory should be retained for the analysis.

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 (1979) 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. In most instances the hydraulic residence time determined using the inflow rate should be used in all calculations. 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 (1982a,1986) 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 the 0.5-m and mid-depth samples. The average phosphorus concentrations found in the waterbody, which include both epilimnetic and hypolimnetic values during the summer weighted for volume, should be compared to the predicted average phosphorus using the procedure developed by Vollenweider (1976) and described for application by Lee *et al.* (1985a,b) 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 paper. 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. Such review may provide information that can be used to demonstrate the need to adjust the sampling program to reliably determine the characteristics of the waterbody being investigated. Lee and Jones (1992) provide guidance on the development of water quality study programs that investigators should review before undertaking a study of this type.

The interpretation of the data in terms of nutrient load-eutrophication response and water quality management should be made through the Vollenweider OECD eutrophication models. Use of these models has been discussed by Rast and Lee (1978), Jones and Lee (1982a,1986), Lee *et al.* (1978), Rast *et al.* (1983), Archibald and Lee (1981), and Lee and Jones (1988,1991a-e).

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 relationship between raw water quality problems or problem-causing organisms and planktonic algal chlorophyll concentrations is 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. As discussed by Jones and Lee (1982b), 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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