



Project Summary

National Surface Water Survey: Western Lake Survey (Phase I — Synoptic Chemistry) Quality Assurance Plan

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The purpose of the National Surface Water Survey of the National Acid Precipitation Assessment Program is to evaluate the present water chemistry of lakes and streams, to determine the status of certain biotic resources, and to select regionally representative surface waters for a long-term monitoring program to study changes in aquatic resources. The Western Lake Survey — Phase I is part of the National Surface Water Survey.

The quality assurance plan and the analytical methods used during Phase I of the Western Lake Survey are based on those used during Phase I of the Eastern Lake Survey; analytical laboratory methods are identical for the two surveys, but some of the field laboratory methods were modified for the West. Sampling protocols are significantly different in that ground access as well as helicopter access was used to collect samples in the West.

Quality assurance requirements and procedures that are unique to the Western Lake Survey — Phase I are treated in detail in the Western Lake Survey Quality Assurance Plan. Quality assurance requirements and procedures that were adopted verbatim from the Eastern Lake Survey — Phase I are referenced in the Western Lake Survey Quality Assurance Plan and are discussed in detail in the Eastern Lake Survey — Phase I Quality Assurance Plan.

This Project Summary was developed by EPA's Environmental Monitoring Systems Laboratory, Las Vegas, NV, to announce key information that is presented in a separate quality assurance plan of the same title (see ordering information at back).

Introduction

The National Acid Precipitation Assessment Program (NAPAP) was initiated at the request of the Administrator of the U.S. Environmental Protection Agency (EPA) to evaluate the extent of the effects of acidic deposition on aquatic resources within the United States. When it became apparent that existing data could not be used to quantitatively assess the present chemical and biological status of surface waters in the United States, the National Surface Water Survey (NSWS) program was incorporated as part of NAPAP to obtain that information. The National Lake Survey (NLS) component of NSWS comprises Phase I — Eastern Lake Survey (ELS-I), Phase I — Western Lake Survey (WLS-I), and Phase II — Temporal Variability.

ELS-I, a synoptic survey of the chemistry of 1,612 representative lakes in the Southeast, Northeast, and Upper Midwest, was conducted to obtain a regional and national data base of water-quality parameters that are pertinent to evaluating the effects of acidic deposition.

Parallel to ELS-I, the WLS-I portion of NSWS is a synoptic survey of 757 lakes

in the West. WLS-I sampling is conducted during fall overturn when chemical variability within a lake is expected to be minimal as a result of circulation within the water column. WLS-I is designed to meet the following objectives for designated regions of the West:

- Determine the percentage (by number and area) and location of lakes that are potentially susceptible to change as a result of acidic deposition and that have low acid-neutralizing capacity (ANC).
- Investigate the relationships among water chemistry, regional acidic deposition patterns, land use, physiographic features, lake morphology, and basin geometry within and among regions.
- Identify smaller subsets of representative lakes for more intensive sampling in future surveys.

WLS-I was designed to provide statistically comparable data that could be extrapolated, with a known degree of confidence, to a regional or national scale. The conceptual approach emphasized that the data would not be used to ascribe observed effects to acidic deposition phenomena; rather, through comprehensive monitoring activities, WLS-I would provide information that could be used to develop correlative, not cause-and-effect, relationships.

The quality assurance (QA) program and the analytical methods for WLS-I are based on those used during ELS-I. The analytical laboratory methods are identical for the two surveys. Some field laboratory methods were modified for WLS-I on the basis of ELS-I experience and on the basis of constraints that resulted from the special geographic limitations associated with the high-altitude lakes in the West. New field laboratory protocols also were added to accommodate changes between ELS-I and WLS-I field sampling methods. Sampling protocols are significantly different in that ground access as well as helicopter access is used to collect samples for WLS-I (Bonoff and Groeger, 1987). The sampling protocols differ from those used during ELS-I because 455 of the WLS-I lakes are within designated wilderness areas that are closed to helicopter access. In order to observe the guidelines and regulations set forth in the Wilderness Act, almost all lakes located within wilderness areas that have been selected for sampling must be sampled by ground crews of the U.S. Department of Agriculture — Forest Service. The ground crews travel to lakes on foot or on horseback. The lakes that are

not in wilderness areas are sampled by helicopter crews under the direction of EPA. The ground sampling protocol developed for use in sampling the restricted-access lakes was first evaluated in a WLS pilot study conducted by EPA's Region VIII office in the autumn of 1984.

A specialized calibration study is included in WLS-I to compare the effects of the two different sampling methods on analytical results. The purpose of the comparison is to derive calibration factors, if necessary, that can be applied to data for samples collected by ground crews so that these data will be equivalent to data for samples collected by helicopter crews. This calibration study is designed to (1) quantify the differences between the two sampling methods, (2) quantify the effects of holding samples for different lengths of time prior to processing, preservation, and analysis, and (3) quantify any significant interlaboratory bias between the two analytical laboratories that analyze WLS-I samples.

Two other studies are being conducted as part of WLS-I. The purpose of one study, the nitrate-sulfate stability study, is to compare sample preservation methods and to study the effects of holding samples for different lengths of time before preserving them. The purpose of the second study, the Corvallis study, is to compare results for splits of the same sample when the splits have been analyzed by different methods. A further purpose of the Corvallis study is to determine whether or not the ICP data can be substituted in the data base if problems arise with the standard analysis. Both studies can provide checks on sampling, processing, and analytical performance.

Quality Assurance Objectives

The statistical design, sampling and analytical methods, and QA activities for WLS-I are structured to meet specific data quality objectives (DQOs) for the measurement of sampling, field laboratory, and analytical laboratory performance. These DQOs are designed to facilitate checking for chemical variability and to provide confidence levels for reporting population estimates.

The primary DQOs are measures of precision (expressed as relative standard deviation), accuracy (expressed as maximum absolute bias), and detectability (expressed as an expected value range and a required detection limit). These DQOs are applied to each parameter measured at the lake sampling site, in the field laboratory, and in the analytical laboratory. Table 1 summarizes the pri-

mary DQOs used for WLS-I. Certain other DQOs also have been considered in the survey design. Completeness (the quantity of acceptable data actually collected in relation to the total quantity that is expected to be collected) is set at 90 percent or better for all variables. Comparability (a measure of the confidence with which one data set can be compared to another) is ensured by requiring that standard procedures be used for laboratory analyses and that a uniform set of units be used for reporting data. The calibration study was performed to ensure that differences in the sampling and on-site analytical procedures used by helicopter crews and ground crews did not reduce data comparability. For WLS-I, representativeness (the degree to which data accurately and precisely represent a characteristic of a population) is maximized by drawing a systematic random sample to ensure good geographical coverage without bias (Landers et al., 1987).

WLS-I is not intended to characterize the chemistry of any given lake spatially or temporally. Therefore, achieving WLS-I objectives does not require that the only sample taken from a lake be completely representative of the lake. In most cases (except for the lakes to be sampled during the calibration study) only one sample per lake is taken during WLS-I. A determination of whether one sample per lake is sufficient to achieve the general objectives of NSWS Phase I, however, can be made from estimates of "within-lake" and "among-lakes" variances. Although some estimates of these variances will be made for WLS-I lakes in accordance with the statistical sampling design, more intensive studies of individual lakes will be necessary to provide more complete data on representativeness.

Although the individual sample is not necessarily representative of the lake, the subset of lakes sampled should be representative of the subregional or regional population of lakes. The systematic sampling design that was adopted for this survey is intended to ensure representativeness at this level.

Monitoring Data Quality

The lakes are selected by means of a systematic, stratified design. There are three stratification factors: regions, subregions, and alkalinity classes. Each stratum is an alkalinity class within a subregion within a region. In the West (NLS Region 4), all three alkalinity classes are found within each of the five sub-

Table 1. Data Quality Objectives For Precision, Accuracy, and Detectability, Western Lake Survey — Phase I

Site ^a	Parameter ^b	Method	Units	Expected Range ^c	Required Detection Limits	Precision Relative Standard Deviation (RSD) Upper Limit (%) ^d	Accuracy Max. Absolute Bias (%)
2, 3	Al, Extractable	Extraction with 8-hydroxyquino- line into MIBK followed by AA ^e (furnace)	mg/L	0.005 - 1.0	0.005	10 (Al conc. >0.01) 20 (Al conc. ≤0.01)	10 20
2, 3	Al, Total	AA ^e (furnace)	mg/L	0.005 - 1.0	0.005	10 (Al conc. >0.01) 20 (Al conc. ≤0.01)	10 20
3	ANC	Titration and Gran analysis	μeq/L	-100 - 1,000	^f	10	10
3	BNC	Titration and Gran analysis	μeq/L	-10 - 150	^f	10	10
3	Ca	AA ^e (flame) or ICP ^g	mg/L	0.5 - 20	0.01	5	10
3	Cl	Ion chromatography	mg/L	0.2 - 10	0.01	5	10
1, 3	Conductance	Conductivity cell and meter	μS/cm	5 - 1,000	^h	2	5
2, 3	DIC	Instrumental (acidification, CO ₂ generation, IR detection)	mg/L	0.05 - 15	0.05	10	10
3	DOC	Instrumental (UV-promoted oxidation, CO ₂ generation, IR detection)	mg/L	0.1 - 50	0.1	5 (DOC conv. >5) 10 (DOC conc. ≤5)	10
3	F ⁻ , Total dissolved	Ion-selective electrode and meter	mg/L	0.01 - 0.2	0.005	5	10
3	Fe	AA ^e (flame) or ICP ^g	mg/L	0.01 - 5	0.01	10	10
3	K	AA ^e (flame)	mg/L	0.1 - 1	0.01	5	10
3	Mg	AA ^e (flame) or ICP ^g	mg/L	0.1 - 7	0.01	5	10
3	Mn	AA ^e (flame) or ICP ^g	mg/L	0.01 - 5	0.01	10	10
3	Na	AA ^e (flame)	mg/L	0.5 - 7	0.01	5	10
3	NH ₄ ⁺	Automated colorimetry (phenate)	mg/L	0.01 - 2	0.01	5	10
3	NO ₃ ⁻	Ion chromatography	mg/L	0.01 - 5	0.005	10	10
1, 2	pH, Field	pH electrode and meter	pH units	3 - 8	—	±0.1 ⁱ	±0.1 ⁱ
3	pH, Analytical laboratory	pH electrode and meter	pH units	3 - 8	—	±0.05 ⁱ	±0.05 ⁱ
3	P, Total	Automated colorimetry (phosphomolybdate)	mg/L	0.005 - 0.07	0.002	10 (P conc. >0.01) 20 (P conc. ≤0.01)	10 20
3	SiO ₂	Automated colorimetry (molybdate blue)	mg/L	0.1 - 25	0.05	5	10
3	SO ₄ ²⁻	Ion chromatography	mg/L	1 - 20	0.05	5	10
2	True color	Comparison to platinum-cobalt color standards	PCU ^j	0 - 200	0	±5 ⁱ	—
2	Turbidity	Instrument (nephelometer)	NTU ^k	2 - 15	2	10	10

^a 1 = lake site, 2 = field laboratory, 3 = analytical laboratory.

^b Dissolved ions and metals are being determined, except where noted.

^c Ranges are for lake waters.

^d Unless otherwise noted, this is the %RSD at concentrations greater than 10 times required detection limits.

^e AA = atomic absorption spectroscopy.

^f Absolute blank value must be ≤10.

^g ICP = inductively coupled plasma atomic emission spectroscopy.

^h Blank must be ≤0.9 μS/cm.

ⁱ Absolute precision goal in terms of applicable units.

^j American Public Health Association platinum-cobalt units.

^k Nephelometric turbidity units.

regions, so the total number of strata in WLS-I is fifteen (see Figure 1).

Several types of QA and quality control (QC) samples are used to ensure that sampling and analytical methods are performed according to specified requirements. QA samples that are introduced in the field or at the field laboratory (field blanks, trailer blanks, field duplicates, and field audits) are analyzed at the field laboratory and at the analytical laboratory. These samples are used to judge the overall performance of WLS-I sampling

and analytical activities and to establish data quality.

QC samples allow field samplers and personnel at the field and analytical laboratories to identify and correct local problems (e.g., providing the analyst with immediate feedback on reagent contamination or questionable instrument performance). Quality control check samples (QCCSs) are used by the helicopter crews to check the calibration of the Hydrolab and to indicate instrument

drift over time. Three types of QC samples (calibration blanks, QCCSs, and trailer duplicates) are used by the field laboratory staff to ensure that instruments and data collection are within specified control limits. Six types of QC samples (calibration blanks, reagent blanks, detection limit QCCSs, low-concentration and high-concentration QCCSs, matrix spikes, and laboratory duplicates) are used by the analytical laboratories to ensure that instruments and data collection are within control limits.

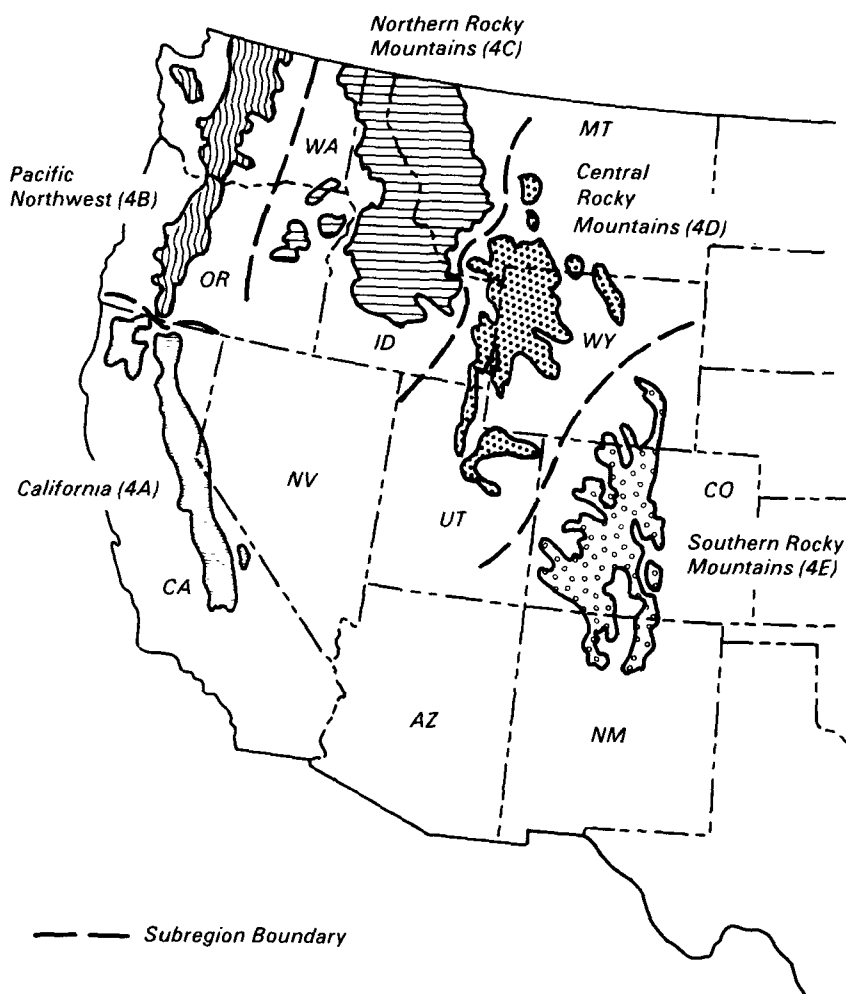


Figure 1. Subregions of the Western United States that are potentially susceptible to acid deposition, Western Lake Survey - Phase I.

Field Operations

Field operations are coordinated at field bases under the supervision of an EPA field base coordinator. One or two helicopter crews (each consisting of a pilot, an observer, a sampler, and a support person) operate from each field base through an EPA duty officer. Each helicopter crew makes one or more excursions to lake sites each day. Ten to fifteen two-person ground crews operate from each base site through a Forest Service field manager. Each helicopter crew samples as many as 10 lakes per day, and each ground crew samples 1 or 2 lakes per day (or per excursion). The field base coordinator and the field manager coordinate the rate of lake sampling so that no more than 30 field samples are processed at a field base on any day. This procedure prevents an overload of samples arriving at the analytical laboratories.

Each field base contains a fully equipped mobile laboratory that is staffed by a field laboratory coordinator, a field laboratory supervisor, and three analysts. The field laboratory coordinator is responsible for the overall operation of the laboratory (e.g., sample tracking and logistics, data, forms, safety). The field laboratory supervisor and the analysts are responsible for sample measurements made at the field base and for sample processing. If necessary, the field laboratory coordinator also assists with sample processing. The aliquots prepared by the field laboratory are described in Table 2.

All field and field laboratory measurements are recorded on the appropriate field forms and in bound log books.

Training

The WLS-I procedure for training the helicopter sampling and field laboratory

personnel is identical to the procedure used during ELS-I. Ground sampling techniques call for new safety and technical considerations, so additional training is provided for ground sampling participants. This training is carried out at Las Vegas and at the field bases and remote sites.

Analytical Procedures and Internal Quality Control

WLS-I analytical procedures and internal QC provisions are identical to those used for ELS-I. These procedures are described fully in the ELS-I Analytical Methods Manual (Hillman et al., 1986) and are summarized in the WLS-I Analytical Methods Manual (Kerfoot and Faber, 1987).

Performance and System Audits

Performance Audit Samples

Field synthetic and field natural audit samples are used to identify problems affecting data quality that may occur during sample processing, shipment, or analysis. These problems could include sample contamination, sample degradation, solvent evaporation, and improper or inaccurate sample analysis.

Waters collected from Big Moose Lake in the Adirondack Mountains, from Lake Superior at Duluth, Minnesota, and from Bagley Lake in the Cascade Range of Washington State are used as natural audit samples for the survey. The waters of Big Moose Lake are acidic; the Lake Superior waters represent a buffered system; and Bagley Lake represents a partially buffered system. Synthetic audit samples are prepared at a central laboratory.

The audit samples are shipped to the analytical laboratories from the field bases as though the audit samples were aliquots of routine lake samples. Every attempt is made to ensure that the analytical laboratory does not recognize the audit samples as different from the routine lake samples.

Data are obtained from the analyses of the field audit samples (1) to judge the performance of the field bases and the analytical laboratories in the processing, shipment, and analysis of samples and (2) to establish a statistically valid estimate of the overall bias and precision of the analyses and of the stability of a typical lake sample.

Acceptance windows are established for the measurement of each audit sample parameter by using a Student's t-statistic test. Acceptance criteria for audit sample values are the same for WLS-I as for ELS-I.

Table 2. Aliquots, Containers, Preservatives, and Corresponding Analyses, Western Lake Survey — Phase I

Aliquot (Container Volume)	Preservative and Description	Analyses
1 (250 mL)	Filtered, preserved with HNO ₃ to pH <2	Ca, Mg, K, Na, Mn, Fe
2 (10 mL)	Filtered, preserved with MIBK-HQ extract	Extractable A1
3 (250 mL)	Filtered, no preservative	Cl ⁻ , total dissolved F ⁻ , SO ₄ ²⁻ , NO ₃ ⁻ , SiO ₂
4 (125 mL)	Filtered, preserved with H ₂ SO ₄ to pH <2	DOC, NH ₄ ⁺
5 (500 mL)	Unfiltered, no preservative	pH, BNC, ANC, conductance, DIC
6 (125 mL)	Unfiltered, preserved with H ₂ SO ₄ to pH <2	Total P
7 (125 mL)	Unfiltered, preserved with HNO ₃ to pH <2	Total Al

Approximately 75 synthetic audit samples and 150 natural-water audit samples are scheduled to be processed during WLS-I. A statistical evaluation of the audit data, including the setting of audit windows, should provide a good estimate of the bias and precision of the analytical methods for each parameter. Furthermore, any change over time in analytical results for the natural-water audit samples without a corresponding change in results for the other audit samples can be attributed to lack of analyte stability. The findings of a comparative study between audit sample types will provide an estimate of the true maximum holding times allowable for each type of analyte.

System Audits

System audits (on-site evaluations) are qualitative evaluations of field and analytical laboratory facilities, equipment, and operations such as record keeping, data reporting, and QC procedures. Each field base and helicopter sampling crew can expect at least one on-site evaluation during the course of the survey. In addition, as many of the 60 ground sampling crews as possible will be evaluated in the field. Each analytical laboratory participating in WLS-I can expect a minimum of two comprehensive, on-site evaluations during the survey.

Data Management

The purpose of the data base management system is to assemble, store, and edit data generated during WLS-I and during other NSWS surveys. The data

base management system also is used to generate basic survey results, to perform certain statistical analyses, and to provide data security.

The WLS-I data are stored in four major data sets: the raw data set, the verified data set, the validated data set, and the final data set. The raw data set is prepared at Oak Ridge National Laboratory (ORNL). The field data and the analytical laboratory data are entered into two separate data sets which are then compared to remove data entry errors. Data evaluation, verification, and validation procedures provide the input from which the verified, validated, and final data sets are prepared.

Data Evaluation and Verification

The field bases and analytical laboratories provide preliminary sample data to the EMSL-LV QA group verbally, by computer, or by telefacsimile. When the field and analytical laboratory data are transmitted through magnetic tapes and the raw data are made available to the EMSL-LV QA group, 100 percent of the data are evaluated and verified on the basis of available QA/QC information. The objective of data verification is to identify data of unacceptable quality and to correct, flag, or target them for possible sample reanalysis or for elimination of the data from future data sets. This data review process is also important in verifying that contractual requirements have been met.

After all data have been reviewed, the analytical laboratories are requested to submit completed copies of data reporting forms that were incomplete when pre-

viously submitted, to submit corrections of previously reported data, to confirm previous results, and to reanalyze certain samples that do not meet QA/QC criteria. The analytical laboratories are directed to respond promptly so that the results can be evaluated in time for them to be useful to the survey.

The verification procedure identifies suspect data and corrects erroneous data. The information is collected by the EMSL-LV QA staff and is placed on magnetic tapes which are sent to ORNL. There, the raw data set is updated to produce the verified data set.

Data Validation

The system of data validation developed for ELS-I is duplicated for WLS-I. The validation process begins concurrently with the verification process. When ORNL provides the ERL-C staff with a computerized version of the verified data set through the National Computing Center at Research Triangle Park (RTP), North Carolina, the validation process can be completed.

Known relationships in aquatic chemistry and limnology are used to identify intrasite sample inconsistencies within data for a set of variables. Intersite validation consists of comparing single site values with values for adjacent sites within a region. Data for groups of sites are compared and mapped to check for consistency. After undergoing this reviewing process, the data are transferred to the validated data set.

Development of a Final Data Set

The calculation of population estimates is difficult if the data set contains missing values. To resolve the problems in the validated data set that result from missing values, a final data set is prepared. This final set is modified by averaging the field routine-duplicate pair values that are within desired precision limits and by replacing analytical values determined to be in error during validation. The values that have been modified for or substituted in the final data set are flagged with the appropriate data qualifiers.

Related Documents

The WLS-I QA Plan described here is the final version of the draft plans that were written before and were modified during WLS-I activities. Quality assurance requirements and procedures that were adopted verbatim from ELS-I are referenced in the WLS-I QA Plan and are described in detail in the ELS-I QA Plan (Droué et al., 1986). Analytical methods

are described in the ELS-I and WLS-I Analytical Methods Manuals (Hillman et al., 1986; Kerfoot and Faber, 1987). ELS-I recommendations that led to WLS-I protocol changes are discussed in the ELS-I QA Report (Best et al., 1987). Only those QA requirements and procedures that are specific to WLS-I are described in the WLS-I QA Plan. A QA report that describes the findings of the survey and the effectiveness of this QA plan will be issued after these factors have been evaluated.

References

- Best, M. D., S. K. Drouse, L. W. Creelman, D. J. Chaloud, 1987. National Surface Water Survey, Eastern Lake Survey (Phase I—Synoptic Chemistry) Quality Assurance Report. EPA 600/4-86-011. U.S. Environmental Protection Agency, Las Vegas, Nevada.
- Bonoff, M. B., and A. W. Groeger 1987. National Surface Water Survey, Western Lake Survey (Phase I—Synoptic Chemistry) Field Operations Report. U.S. Environmental Protection Agency, Las Vegas, Nevada.
- Drouse, S. K., D.C. Hillman, L. W. Creelman, and S. J. Simon, 1986. National Surface Water Survey, Eastern Lake Survey (Phase I—Synoptic Chemistry) Quality Assurance Plan. EPA 600/4-86-008. U.S. Environmental Protection Agency, Las Vegas, Nevada.
- Hillman, D. C., J. F. Potter, and S. J. Simon, 1986. National Surface Water Survey, Eastern Lake Survey (Phase I—Synoptic Chemistry) Analytical Methods Manual. EPA 600/4-86-009. U.S. Environmental Protection Agency, Las Vegas, Nevada.
- Kerfoot, H. B., and M. L. Faber, 1987. National Surface Water Survey, Western Lake Survey (Phase I—Synoptic Chemistry) Analytical Methods Manual. U.S. Environmental Protection Agency, Las Vegas, Nevada.
- Landers, D. H., J. M. Eilers, D. F. Brakke, W. S. Overton, P. E. Kellar, M. E. Silverstein, R. D. Schonbrod, R. E. Crowe, R. A. Linthurst, J. M. Omernik, S. A. Teague, and E. P. Meier, 1987. Characteristics of Lakes in the Western United States. Volume I. Population Descriptions and Physico-Chemical Relationships. EPA/600/3-86/054a. U.S. Environmental Protection Agency, Washington, D.C.

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The complete report, entitled "National Surface Water Survey, Western Lake Survey (Phase I—Synoptic Chemistry) Quality Assurance Plan," (Order No. PB 87-214 862/AS, Cost: \$18.95, subject to change) will be available only from:

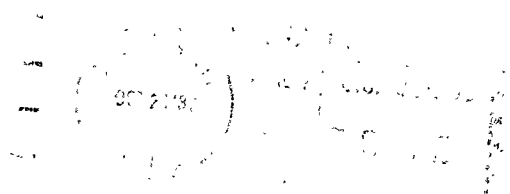
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