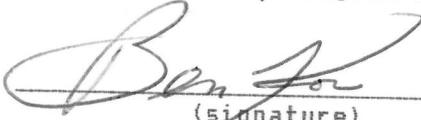
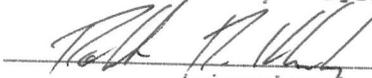


QUALITY ASSURANCE PROGRAM  
FOR  
TOXIC SUBSTANCE DETECTION AND EARLY WARNING  
FOR THE RUSSIAN RIVER

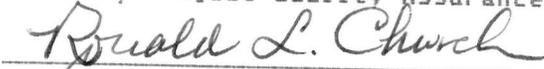
Benjamin D. Kor, Project Director

  
(signature)

Robert R. Klamt, Project Manager

  
(signature)

Ronald L. Church, Project Quality Assurance Officer

  
(signature)

California Regional Water Quality Control Board  
North Coast Region  
1440 Guerneville Road  
Santa Rosa, California 95401

March 2, 1987

Primary funding for this study has been provided by the California State Water Resources Control Board using Section 205(j) grant funds made available by the U.S. Environmental Protection Agency. This does not signify that the contents necessarily reflect the views and policies of the U.S. Environmental Protection Agency or the California State Water Resources Control Board, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

1. Project Name:  
Toxic Substances Detection and Early Warning for the Russian River
2. Project Requested By:  
State Water Resources Control Board, North Coast Region (RB), Section 205(j) Water Quality Management and Planning Program
3. Date of Request:  
Workplan dated May 14, 1985.
4. Date of Project Initiation: expected to begin March 15, 1986
5. Project Officers:  
Project Director - Benjamin D. Kor, RB Executive Officer  
Project Manager - Robert R. Klamt, RB Environmental Specialist
6. Quality Assurance Officer:  
Ronald L. Church, RB Environmental Specialist
7. Project Description

A. Objective and Scope Statement:

This project will investigate the findings of occasional low levels of organic chemicals and heavy metals in the Russian River through a water quality assessment program and will evaluate and recommend an early warning network for use by Russian River water purveyors serving approximately 500,000 people. The ultimate goal of this program is the development of an implementable early warning program for alerting Russian River water users of the presence of toxic substances in the Russian River. Specific objectives are:

1. the implementation of macro-reticular resin sampling methodology developed by a previous 205(j) project,
2. testing and assessment of an early warning system to detect toxic substances in the Russian River,
3. recommendations for the implementation of a toxic substances early warning network for the Russian River.

Objective 1 is the specific objective to which this quality assurance program pertains. This quality assurance program deals only with the monitoring associated with that objective.

B. Data Usage:

Data will be used primarily to assess the quality of the Russian River and the adequacy of a motion analysis detection system for detecting toxic substances in surface waters. Additional uses may include spill response by the Regional Board and other agencies, and regulatory activities arising from illegal discharges and/or spills of toxic substances into the Russian River. To the extent possible, all water quality related data generated by this project will be submitted to the State Water Resources Control Board in a timely manner and in a format compatible with the federal STORET data management system.

C. Monitoring Network Design and Rationale:

The sampling involves two phases: a development phase and an implementation phase. Initial monitoring will be at a prototype early warning site in parallel with the motion analysis system. Once the development phase is completed, monitoring will occur upstream and downstream of selected urbanized and industrialized areas of the Russian

River basin. Those areas will be selected based on likelihood of effects on the river (Figure 1). The purpose of monitoring in those cases will be to describe the water quality as regards toxic chemicals in the immediate vicinity of those areas.

D. Monitoring Parameters and their Frequency of Collection:

Resin column samples will be analyzed for heavy metals and complex organic chemicals. Initial sampling frequency is planned for twice monthly at the prototype early warning site. Following implementation of the methodology, sampling is expected to occur at twelve sites (Figure 1) on a frequency of three times per sampling period. The actual number of samples will be determined on the basis of budget constraints.

E. Parameter Table

All samples will be obtained by resin columns and preserved by freezing until elution/extraction and analysis. The metals samples will be eluted/extracted with acid depending on the resin utilized: Chelex 100, use 2.5 N HNO<sub>3</sub>; AG 1X-8, use 4.0 M HCl; Duolite S-5B7, use 50:50 solution of 2.0 M HCl and 0.1 N HNO<sub>3</sub>. The eluted/extracted sample concentrate is stable for up to 6 months, however will be analyzed within 15 days.

<u>Parameter</u>	<u>Sample Matrix</u>	<u>Analytical Method Reference</u>	<u>Sample Preservation</u>	<u>Holding Time</u>
Arsenic	I	EPA 206.2, 200.7	I	< 10 days
Cadmium	I	EPA 213.2, 200.7	I	< 10 days
Chromium	I	EPA 218.2, 200.7	I	< 10 days
Copper	I	EPA 220.2, 200.7	I	< 10 days
Lead	R	EPA 239.2, 200.7	F	< 10 days
Mercury	E	EPA 245.2	R	< 10 days
Selenium	S	EPA 270.3, 200.7	E	< 10 days
Vanadium	I	EPA 286.2, 200.7	E	< 10 days
Zinc	N	EPA 289.2, 200.7	Z	< 10 days
Chlorinated Pesticides	I	EPA 608	E	< 2 days
Organophosphate Pesticides	I	APHA 509A	I	< 2 days
Phenoxy Herbicides	I	APHA 509B	I	< 2 days
Chlorinated Phenols*	I	Chau & Coburn, 1974	I	< 2 days

\* J. Assoc. Off. Ann. Chem., 57 (2): 389-393. Determination of pentachlorophenol in natural and waste waters.

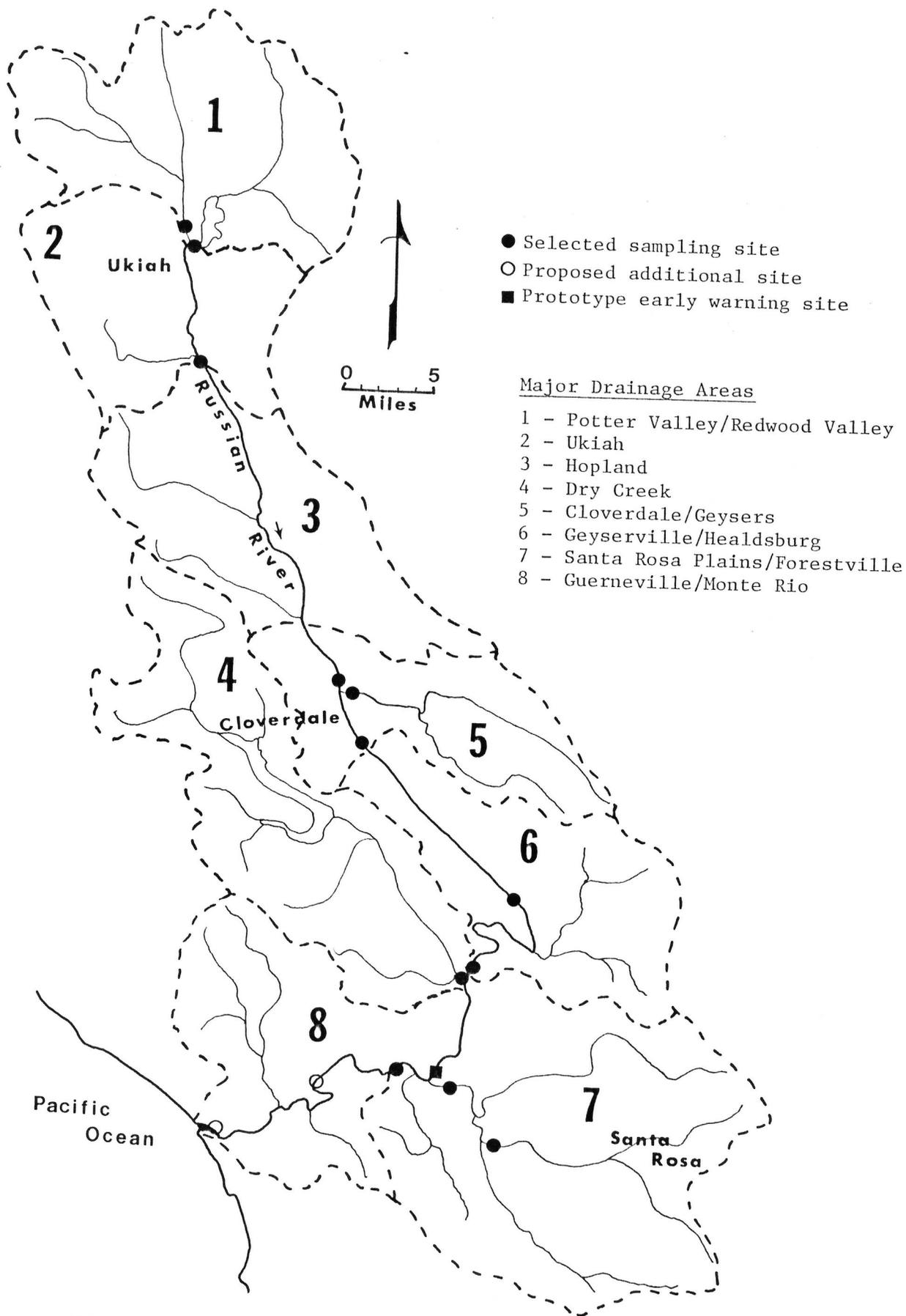


Figure 1. Major drainage areas and sampling sites for "Toxic Substance Detection and Early Warning for the Russian River," Russian River basin, California.

8. Project Fiscal Information:  
 The original budget appears on page 20 of the previously-referenced workplan dated May 14, 1985. An updated budget is attached as Appendix A.

9. Schedule of Tasks and Products  
 The project workplan was approved by the Regional Board on May 23, 1985, and the State Board at its June 5 & 6, 1985, workshop.

The following table relates to the monitoring section of the project.

SCOPE	FY 85-86					FY 86-87					FY 87-88														
	F	M	A	M	J	J	A	S	O	N	D	D	J	F	M	A	M	J	J	A	S	O	N	D	J
Purchase Resins					**																				
Prepare Resins										**															
Construct Samplers					**																				
Preliminary Testing										*****															
Monitoring																									
Analysis																									
STORET Data Input													**		**		**			**		**		**	
Report Preparation																									
Draft Preparation																									
Draft Peer Review																									
Final Preparation																									

10. Project Organization and Responsibility  
 An organizational chart is provided as Figure 2. The following is a list of key project personnel and their corresponding responsibilities:

Regional Board/State Board Coordinator - Dan Otis, Division of Water Quality, State Water Resources Control Board

Regional Board Policy Implications - Benjamin D. Kor, Executive Officer, North Coast Regional Water Quality Control Board

Overall Project Coordination - Robert R. Klamt, Project Manager, North Coast Regional Water Quality Control Board

Overall Quality Assurance - Ronald L. Church, Environmental Specialist, North Coast Regional Water Quality Control Board

Contract Laboratory Analysis and QC - Greg Anderson, Laboratory Director, Anatec Laboratories, Inc.

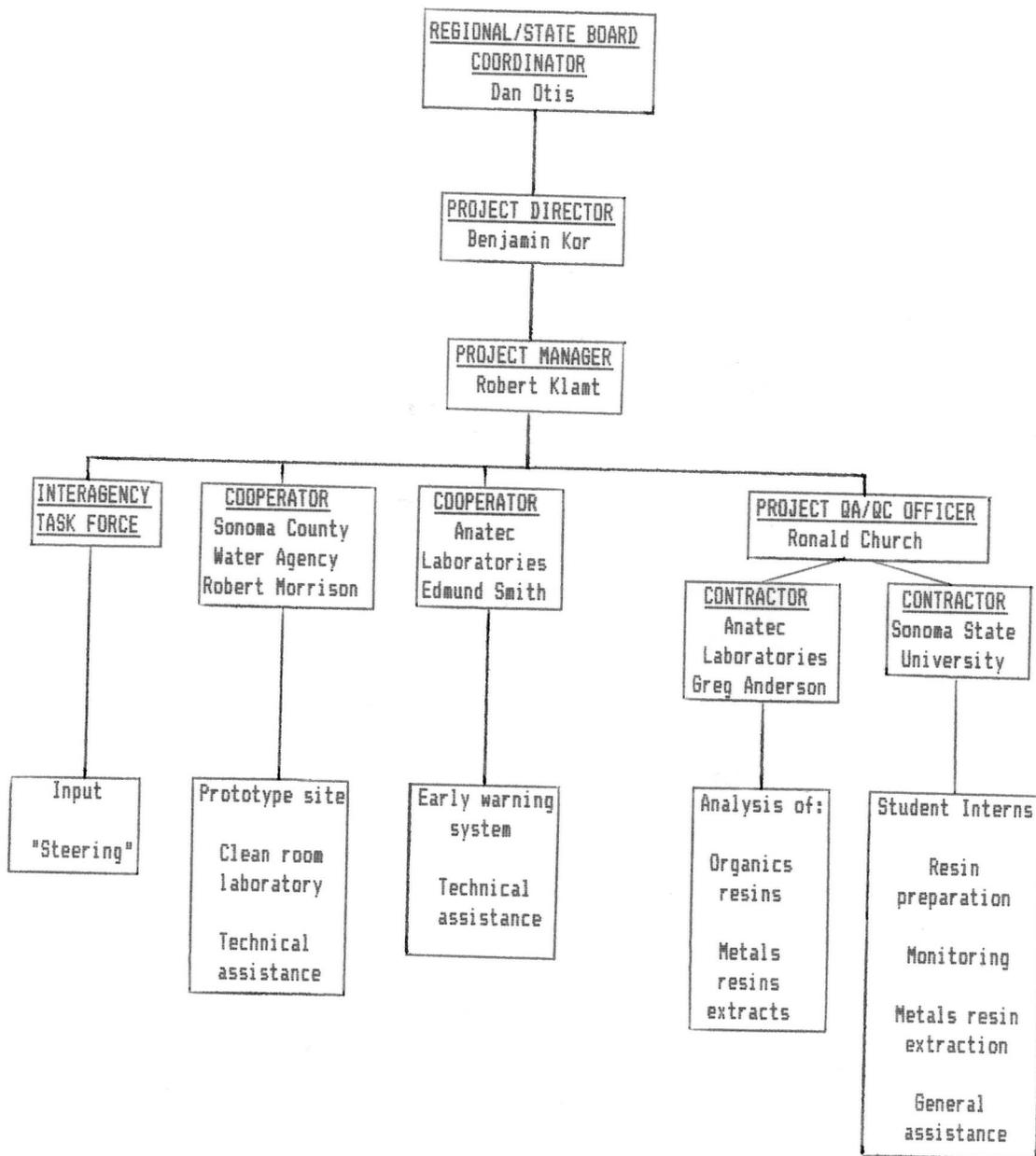


Figure 2. Organizational chart for Section 205(j) "Toxic Substance Detection and Early Warning for the Russian River."

11. Data Quality Requirements and Assessments

<u>Parameter</u>	<u>Sample Matrix</u>	<u>Detection Limit</u>	<u>Estimated Accuracy</u>	<u>Accuracy Protocol</u>	<u>Estimated Precision</u>	<u>Precision Protocol</u>
Arsenic	acid extract	5 ug/l	± 20%		± 20%	
Cadmium	acid extract	5 ug/l	± 20%		± 20%	
Chromium	acid extract	10 ug/l	± 20%		± 20%	
Copper	acid extract	5 ug/l	± 20%		± 20%	
Lead	acid extract	10 ug/l	± 20%	S	± 20%	S
Mercury	acid extract	1 ug/l	± 20%	E	± 20%	E
Selenium	acid extract	20 ug/l	± 20%	"A"	± 20%	"B"
Vanadium	acid extract	50 ug/l	± 20%	B	± 20%	B
Zinc	acid extract	20 ug/l	± 20%	E	± 20%	E
Chlorinated Pesticides	resin	5 ug/L	± 20%	L	± 20%	L
				O		O
				W		W
Organophosphate Pesticides	resin	5 ug/L	± 20%		± 20%	
Phenoxy Herbicides	resin	2 ug/L	± 20%		± 20%	
Chlorinated Phenols	resin	5 ug/L	± 20%		± 20%	

A. Accuracy Protocol: Generally accepted methods of accuracy assessment will be used in the field and laboratory. Field blanks, method blanks, and spikes will occur on a 10% frequency. Standard calibration/standardization procedures will be used by the laboratory for AA, ICP, and GC measurements. Additionally, internal standards will be used on the GC analyses. External reference samples will be analyzed by the contract laboratory at least every three months.

B. Precision Protocol: Generally accepted methods of assessment for precision will be employed. Side-by-side duplicates will be submitted to the laboratory on a 10% sample frequency. Additionally, the laboratory will perform replicate analyses on a by-batch basis or 10% frequency (whichever is more frequent).

Data Representativeness:

Initial sampling will be to test and develop the sampling methodology. Later monitoring will be for the purposes of testing and cross-checking the early warning system and of describing the overall quality of the Russian River with respect to heavy metals and complex organic chemicals. Site-specific monitoring will be designed to provide information on the quality of the river regarding those constituents upstream and downstream of an industrialized area. Monitoring will occur over a period of up to seven (7) days with river water pumped for appropriate periods through the resin columns at frequent intervals (5-15 minutes). This will effectively integrate the constituent concentrations over the period for each site and increase the likelihood of detecting short-term pulses of chemicals. More frequent sampling will be conducted if results from the one-week sampling indicate presence of contaminants.

Data Comparability:

All results will be presented in terms of concentration of constituent in the water for the period sampled. The data will be comparable to like data from the project, however will not be directly relatable to standard grab sample data. The data will be comparable to composite monitoring data to some degree.

Data Completeness:

The initial sampling will be used to test and develop the sampling methodology. Additional data collected later in the project will satisfy the objective of providing a cross-check against the early warning system, as well as providing additional information on the general health of the Russian River.

12. Sampling Procedures:

Sampling procedures will be as specified in the attached document titled "A Guide to the Preparation and use of Selected Macroreticular Resins for Environmental Monitoring: North Coast Region."

13. Sample Custody Procedures:

It is anticipated that no more stringent custody will be needed than the procedures specified in the attached document titled "A Guide to the Preparation and use of Selected Macroreticular Resins for Environmental Monitoring: North Coast Region."

14. Calibration Procedures and Preventative Maintenance:

Regarding contract laboratory procedures, reference is made to Anatec Laboratories, Inc. "Response to Bid" for the FY 1985-86 general laboratory contracts for the North Coast Region, and contained in the Regional Board files. Resin sampling equipment will be maintained as specified in the attached document titled "A Guide to the Preparation and use of Selected Macroreticular Resins for Environmental Monitoring: North Coast Region."

15. Documentation, Data Reduction, and Reporting

A. Documentation:

Sampling conditions will be recorded in hard-bound data log books at the time of sampling. All resin column preparation and extractions will likewise be recorded in hard-bound log books. Minimum documentation will be sampler/analyst's name, date and time, activity or procedure, and conditions at time of activity. Documentation procedures are specified in the attached document titled "A Guide to the Preparation and use of Selected Macroreticular Resins for Environmental Monitoring: North Coast Region."

B. Data Reduction and Reporting:

Quality control procedures (previously mentioned in this plan) and analytical calculation procedures are referenced in the Anatec Laboratories, Inc. "Response to Bid" for the FY 1985-86 general laboratory contracts for the North Coast Region, and contained in the Regional Board files. Reports received from the laboratory will be reviewed by the Project Manager and submitted for input into a computerized database by another person. Data verification will be performed by a third individual. In addition, data will be transferred to appropriate forms for inclusion into the STORET system, with data verification performed by still another person.

Computerized statistical analyses will follow input to the database. Formal reporting of the data will be included in the quarterly reports for the project as a whole. Those reports may receive in-house and peer review prior to publication.

16. Data Validation

Data validation begins with the accuracy and precision protocols outlined in Section 11 (pages 7 & 8) of this plan. Prior to acceptance of the data and use in a report, statistical analyses may be performed to determine "outliers." The sampling and resin handling documentation for each batch of samples, as well as the accuracy and precision data, will be used to determine if outliers can be explained. If not, then re-analysis of the extracts will be performed. In the event the re-analysis data are consistent with the original analyses, the "outliers" will be accepted as valid data. Data validation procedures are outlined for computer input in Section 15.B., above.

17. Performance and System Audits

External audit samples will be analyzed by the contract laboratory on a quarterly basis. Systems audits will be performed prior to monitoring and on a quarterly basis thereafter by the interagency Task Force to determine the capabilities of the sampling and analysis group with regards to the sampling, sample and extract handling, and adherence to the Quality Assurance Project Plan.

18. Corrective Action

Errors and/or inconsistencies in sample collection, sample and extract handling, analysis of extracts, data handling, and data reduction and interpretation as identified by the above procedures will be referred to appropriate levels of management. The basic protocol shall be to fully document and refer sample collection and handling problems to the

Project Manager, and extract handling problems to the Project Quality Assurance Officer. In the event extraction problems can not be resolved at that level, they will be referred to the Project Manager, who may consult with the Contract Laboratory Analysis and QC Officer.

Analysis problems at the contract laboratory will be referred from the bench level chemists through the appropriate lab supervisor, then to the laboratory supervisor. In the event problems are not resolved, the laboratory supervisor will refer the problem to the laboratory director (Contract Laboratory Analysis and QC Officer) and thence, the Project Manager.

Data handling, reduction, and interpretation problems will be referred to the Project Manager who may consult with the Project Director on policy matters, the contract laboratory director on analytical questions, or the Project Quality Assurance Officer, the Task Force, or the Department of Health Services on other matters.

#### 19. Reports

Quarterly progress reports and interim reports will be presented to the Regional Board and interested parties as outlined in the Project Workplan, and will be made available to the public upon request.

APPENDIX A

Revised budget for 205(j) project, "Toxic Substance Detection  
and Early Warning for the Russian River" (rev. 11-17-86).

RUSSIAN RIVER PROJECT BUDGET SUMMARY

ITEM	85-86	86-87	87-88	TOTAL
STAFF YEARS	0	0	0	\$0
EQUIPMENT	3350	0	0	\$3,350
SUPPLIES	6089	2632	2000	\$10,721
CONTRACTS				
CSU SONOMA	1323	30000	7988	\$39,311
LABORATORY	29500	40000	15118	\$84,618
TOTAL DIRECT	40262	72632	25106	\$138,000
MATCH				
SCWA STAFF	5920	2560	0	\$8,480
SCWA MATERIALS	5000	0	0	\$5,000
ANATEC STAFF	7244	10620	6000	\$23,864
ANATEC MATERIALS	0	1000	0	\$1,000
REG. BD. STAFF	2552	3276	1828	\$7,656
TOTAL MATCH	20716	17456	7828	\$46,000
=====				
GRAND TOTALS	60978	90088	32934	\$184,000