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BERKELEY LAB

ERNEST ORLANDO LAWRENCE BERKELEY NATIONAL LABORATORY
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1 Cyclotron Road, MS936B
Berkeley, CA 94720
510.486.7391 (voice) * 510.486.4386 (fax)

CFO/Sponsored Projects Office

April 15, 1999

CALFED Bay-Delta Program Office
Attn: Wendy Halverson Martin
Restoration Coordinator
1416 Ninth Street, Suite 1155
Sacramento, CA 95814

REFERENCE REPLY: LBNL Proposal BG 99-210 (00)
Response to CALFED Bay-Delta Program 1999 Proposal Solicitation

Enclosed for your consideration is an original and nine (9) copies of the subject proposal along with electronic copy of text and tables as requested. This proposal is submitted on behalf of the Ernest Orlando Lawrence Berkeley National Laboratory (LBNL):

Title: Real-Time Sensors for Mercuric and Selenate Ions Utilizing Templated Polymer Technology

Principal Investigator: Richard H. Fish, PhD.

Total Amount Requested: $793, 871.00

Period Requested: 2 Years

Type of Request: New

LBNL is operated by The Regents of the University of California for the Department of Energy (DOE) under prime contract DE-AC03-76SF00098 and all work is conducted under the terms of that contract and subject to the approval of DOE. This proposal will be submitted to DOE for approval.

Please note that we have had discussions this week with Ms. Jo Turner and Ms. Nan Yoder of CALFED with respect to determining the appropriate contract terms and conditions to be utilized if we are favored with an award under this program. It is our understanding that the applicable terms and conditions will be determined by the source of funds used to fund the specific project. Specifically, Ms.Turner and Ms.Yoder confirmed the following guidelines in determing the appropriate terms and conditions:

FEDERAL FUNDS: If CALFED makes an award derived from federal funds, a federal interagency agreement would be the appropriate contractual vehicle used for performing the work at LBNL. The agreement would be between the federal sponsor and DOE. We can provide additional guidance if an award is contemplated. It should be noted that such agreement must include the following language:

> "This agreement is entered into pursuant to the Authority of the Economy Act of 1932, as amended (31 U.S.C. 1535), and adheres to Federal Acquisition Regulation (FAR) 6.002 and other applicable Federal Laws and Regulations. To the best of our knowledge, the work requested will not place the DOE and its contractor in direct competition with the private sector."

STATE OF CALIFORNIA FUNDS: If CALFED'S funds for an award are derived from California state funds, Ms. Yoder expressed an interest in reviewing and possibly utilizing the master terms and conditions, or a variation thereof, currently being finalized between DOE and the California Energy Commission (CEC) for several CEC awards to LBNL. It was agreed that LBNL would provide a copy of the final CEC/LBNL agreement for CALFED's review at the time of a CALFED award to LBNL. It should be noted that the proposed CEC/LBNL agreement has been in negotiations over an extended period of time and is being reviewed by the California General Services Administration for their final approval.

As soon as a funding decision is made, please contact the undersigned wherein we will be able to mutually determine the appropriate contracting mechanism.

In addition, please note that LBNL intends to award a two-year subcontract to John Hopkins University (Applied Physics Laboratory) to support the efforts of LBNL's Dr. Richard Fish, at a cost of $199,691.00 (see enclosed budgets).

If you have any questions regarding this submission, please feel free to call me on (510) 486-7391 or Facsimile No. (510) 486- 4386.

Sincerely,

Richard W. Wilson
Contracting Officer
E-Mail Address: RWWilson@lbl.gov

Enclosures

cc: R. Fish, w/o Enclosures
M. Beck, w/o Enclosures
G. Burns, w/o Enclosures

Proposal Title: Real-Time Sensors for Mercuric and Selenate Ions Utilizing Templated Polymer Technology
Applicant Name: Richard Wilson
Mailing Address: Lawrence Berkeley National Laboratory, MS 936B, Berkeley, CA 94720
Telephone: (510) 486-7391
Fax: (510) 486-4386
Email: rwwilson@lbl.gov

Amount of funding requested: $ 793,871 for 2 years

Indicate the Topic for which you are applying (check only one box).

- ☐ Fish Passage/Fish Screens
- ☐ Habitat Restoration
- ☐ Local Watershed Stewardship
- ☑ Water Quality
- ☐ Introduced Species
- ☐ Fish Management/Hatchery
- ☐ Environmental Education

Does the proposal address a specified Focused Action? X yes ____ no

What county or counties is the project located in? Merced County

Indicate the geographic area of your proposal (check only one box):

- ☐ Sacramento River Mainstem
- ☐ Sacramento Trib: ________
- ☑ San Joaquin River Mainstem
- ☐ San Joaquin Trib: ________
- ☐ Delta: ________
- ☐ East Side Trib: ________
- ☐ Suisun Marsh and Bay
- ☐ North Bay/South Bay: ________
- ☐ Landscape (entire Bay-Delta watershed)
- ☑ Other: Cache Creek, San Joaquin West-side Trib.

Indicate the primary species which the proposal addresses (check all that apply):

- ☐ San Joaquin and East-side Delta tributaries fall-run chinook salmon
- ☐ Winter-run chinook salmon
- ☐ Late-fall run chinook salmon
- ☐ Delta smelt
- ☐ Splittail
- ☐ Green sturgeon
- ☑ Migratory birds
- ☐ Other:
- ☐ Spring-run chinook salmon
- ☐ Fall-run chinook salmon
- ☐ Longfin smelt
- ☐ Steelhead trout
- ☐ Striped bass
- ☐ All chinook species
- ☑ All anadromous salmonids

Specify the ERP strategic objective and target(s) that the project addresses. Include page numbers from January 1999 version of ERP Volume I and II:

Prospective, pages 4-5. Comprehensive Monitoring, pages 7-9.

Contaminants: Program Action 1B, page 114. These ERP strategic objectives and targets synergize the CALFED Water Quality plan on Selenium and Mercury.

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Proposal Title:	Real-Time Sensors for Mercuric and Selenate Ions Utilizing Templated Polymer Technology
Applicant Name:	Richard Wilson
Mailing Address:	Lawrence Berkeley National Laboratory, MS 936B, Berkeley, CA 94720
Telephone:	(510) 486-7391
Fax:	(510) 486-4583
Email:	rwwilson@lbl.gov

Amount of funding requested: $ 793,871 for 2 years

Indicate the Topic for which you are applying (check only one box).

- ☐ Fish Passage/Fish Screens
- ☐ Habitat Restoration
- ☐ Local Watershed Stewardship
- ☑ Water Quality
- ☐ Introduced Species
- ☐ Fish Management/Hatchery
- ☐ Environmental Education

Does the proposal address a specified Focused Action? X yes ____ no

What county or counties is the project located in? Merced County

Indicate the geographic area of your proposal (check only one box):

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- ☐ Sacramento Trib: ____
- ☑ San Joaquin River Mainstem
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Indicate the type of applicant (check only one box):

- ☐ State agency
- ☐ Public/Non-profit joint venture
- ☐ Local government/district
- ☐ University
- ☐ Federal agency
- ☐ Non-profit
- ☐ Private party
- ☑ Other: National Laboratory

Indicate the type of project (check only one box):

- ☐ Planning
- ☑ Monitoring
- ☐ Research
- ☐ Implementation
- ☐ Education

By signing below, the applicant declares the following:

1.) The truthfulness of all representations in their proposal;

2.) The individual signing the form is entitled to submit the application on behalf of the applicant (if the applicant is an entity or organization); and

3.) The person submitting the application has read and understood the conflict of interest and confidentiality discussion in the PSP (Section 2.4) and waives any and all rights to privacy and confidentiality of the proposal on behalf of the applicant, to the extent as provided in the Section.

Richard Wilson

Printed name of applicant

Richard Wilson

Signature of applicant

Title Page

Project Title: Real-Time Sensors for Mercuric and Selenate Ions Utilizing Templated Polymer Technology

Applicants: Lawrence Berkeley National Laboratory
Attn: Richard Wilson
1 Cyclotron Road, Berkeley, CA 94720

PI: Richard H. Fish, PhD.
(510) 486-4850 (Phone); (510) 486-7303 (FAX); rfish@lbl.gov

Collaborator within LBNL:
Nigel W.T. Quinn, PhD, P.E.
(510) 486-7056, nwquinn@lbl.gov

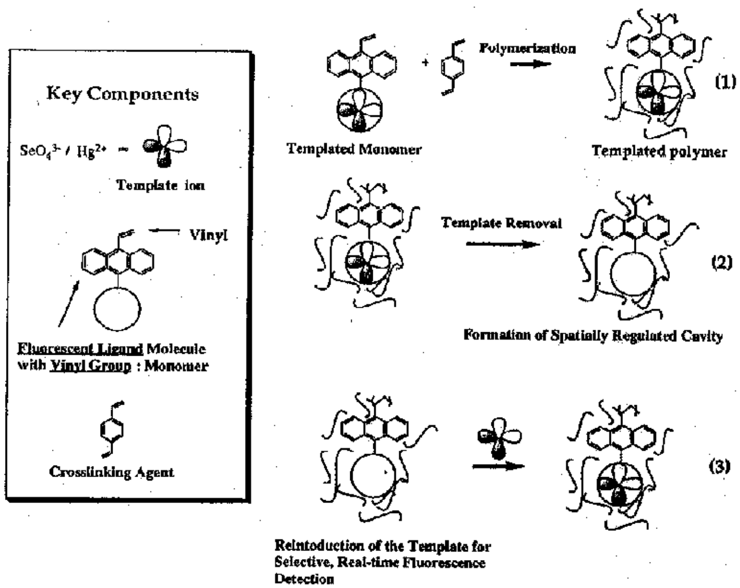
Subcontractor to LBNL:
Johns Hopkins University
Applied Physics Laboratory
Laurel, MD 20723-6099
*George M. Murray, PhD
(443) 778-3882 (Phone) (443) 778-6914 (FAX
murragm1@aplcomm.jhuapl.edu

Executive Summary

Real-time management of west-side San Joaquin selenium drainage and management of Sacramento Basin mercury discharges are specified goals of the CALFED Water Quality Program. A demonstration of the capabilities and benefits of real-time salinity management by the SJRMP Water Quality Subcommittee has received funding by CALFED. Salinity can be measured in real-time through the real-time forecasting of the selenium (selenate, SeO_4^{3-}) concentrations. Therefore, water quality cannot be performed with the requisite degree of accuracy for compliance purposes without the deployment of a continuously recording selenium sensor device. In the Grassland Bypass Project, neither electrical conductivity or flow are adequately correlated with selenium concentrations to be useful in selenium load forecasting. In the case of mercury mine discharge management from sources in Cache Creek, lack of a real-time sensor for continual mercury (Hg^{2+} [or CH_3Hg^+]) analysis compromises the development and implementation of the Total Mass Daily Load (TMDL) program actions (the Cache Creek Hg Group was just funded by CALFED for this and other ecological studies), specified amongst the CALFED water quality actions. The project's primary benefit is to increase the frequency of meeting San Joaquin and Sacramento River water quality objectives for $SeO_4^{3-}$and Hg^{2+} ion concentrations.

Thus, this proposed project is focused on developing robust, real-time, selective sensors for mercury (Hg^{2+}) monitoring in Cache Creek in the Sacramento River Basin and, as well, selenium (selenate, SeO_4^{3-}) monitoring in the San Joaquin River and its west-side tributaries. Research, development, and deployment phases of the proposed two year project involves the following tasks for application of state-of-the-art metal/metalloid ion templated polymer technology, previously used to develop a real-time, selective sensor for lead ions (Pb^{2+}), to novel, templated polymer sensors for Hg^{2+} and SeO_4^{3-} and includes: **(a)** Synthesis of the Hg^{2+} and SeO_4^{3-} monomer complexes containing designer ligands for optical and electrochemical detection; **(b)** Polymerization of these templated monomer complexes, to create several novel, templated polymers selective to reintroduced Hg^{2+} or SeO_4^{3-} ions; **(c)** Fabrication of fiber optic or electrode probes for field deployment of real-time, selective sensors for Hg^{2+} and SeO_4^{3-} ions; **(d)** Determination of the selectivity and analytical sensitivity parameters (parts per trillion range), and; **(e)** field deployment of these real-time, selective sensor devices for long-term Hg^{2+} and SeO_4^{3-} ion monitoring at environmental sites of interest. See Scheme 1, for an explanation of the imprinted polymer concept.

Templated Polymer Technique



Scheme 1

What is clearly evident is that without real-time sensors for Hg^{2+} and SeO_4^{3-} ions, or for that matter any toxic metal ion of environmental interest, no real-time management for acute toxicity monitoring to mitigate the effects of the high concentrations of these metal ions will be viable. The primary stressor addressed by the program is contaminants entering the lower San Joaquin River and Cache Creek, which empties into the Sacramento River. The primary ecosystem and water quality benefits of sensor development will include: **(a)** allow real-time management of selenium discharges into the San Joaquin River and **(b)** allow improved management of mercury loads from mines in the Cache Creek watershed (*see attached letters from constituency groups supporting this proposal and the concept of real-time sensors for real-time ecosystem management).

Secondary benefits from selective Hg^{2+} and SeO_4^{3-} sensor development are a likely reduction in the number and/or magnitude of violations of the EPA selenium concentration objectives for the San Joaquin River downstream of the Merced River and of EPA mercury objectives in Cache Creek. Species and species groups benefiting from reduced selenium and mercury concentrations besides chinook salmon and steelhead trout, are delta smelt, longfin smelt, splittail, white and green sturgeon, striped bass, marine/estuarine fishes and large invertebrates, and Bay-Delta aquatic foodweb organisms.

Project Description

Project Description and Approach

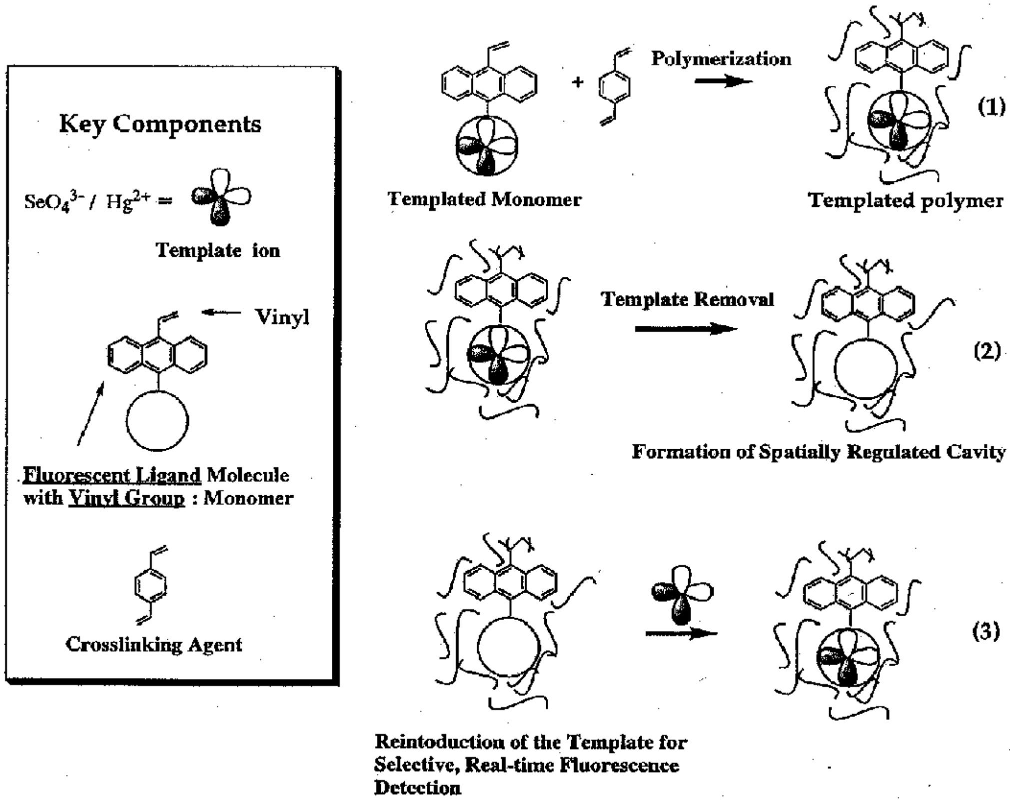
The goal of the proposed project is to develop real-time, selective sensors for mercury (Hg^{2+}) monitoring in Cache Creek in the Sacramento River Basin and selenium (selenate, SeO_4^{3-}) monitoring in the San Joaquin River and its west-side tributaries. Research, development, and deployment phases of the proposed two year project involve the following tasks for application of state-of-the-art metal/metalloid ion templated polymer technology, previously used to develop a real-time, selective sensor for lead ions (Pb^{2+}), to new, templated polymer sensors for Hg^{2+} and SeO_4^{3-} and includes: **(a)** Synthesis of Hg^{2+} and SeO_4^{3-} monomer complexes containing designer ligands for optical or electrochemical detection; **(b)** Polymerization of these templated monomer complexes, to create several new, templated polymers selective to reintroduced SeO_4^{3-} or Hg^{2+} ions; **(c)** Fabrication of fiber optic/electrode probes for field deployment of real-time, selective sensors for Hg^{2+} and SeO_4^{3-} ions and; **(d)** Determination of the selectivity and analytical sensitivity parameters and; **(e)** field deployment of these real-time, selective sensor devices for long-term $Hg^{2+}$and SeO_4^{3-} ion monitoring at designated environmental sites.

Application of Templated Polymer Technology.

The concept of selective, metal/metalloid ion templated polymers has been studied by Fish and co-workers (Hg^{2+} and copper (Cu^{2+}) amongst others [(2)], while Murray and co-workers have designed, developed, and deployed instruments for field optical and electrochemical sensing of metal ions, such as lead (Pb^{2+}) and uranium (UO_2^{2+}), as well as organic compounds, such as the hydrolysis product of the nerve agent, soman [(3)]. The basic templated polymer premise **(Figure 1)** involves: **(Cartoon 1)** forming a imprinted/templated metal/metalloid ion-monomer complex followed by co-polymerization with a crosslinking agent, such as divinylbenzene, to form a templated metal/metalloid ion-polymeric ligand matrix (bulk materials). The ultimate goal **(Cartoon 2)** of the templated metal/metalloid ion-polymeric ligand complex, thus formed, is to remove the template ion by, for example, acid treatment, and the subsequent reintroduction **(Cartoon 3)** of the metal/metalloid ion used as the template allows repeated recognition, in a selective manner, when other ions compete with it for the same polymeric, spatially regulated ligand site. *Thus, selectivity for a specific metal/metalloid ion can be tailored by providing templated polymers with spatially regulated sites and complexing ligands so arranged as to match the charge, coordination number, coordination geometry, and ionic radius of the toxic metal /metalloid ions to be detected.*

Figure 1

Templated Polymer Technique



Many sensor parameters that are critical for performance; i.e., selectivity, sensitivity, and lack false positive responses, are not well developed and, apart from Murray's sensor devices, efforts to develop these metal ion sensors have not been successful for the following reasons:

1. Low selectivity: Competition with other metal ions that might bind to the ligand.
2. Low sensitivity: parts per million range, rather than the parts per trillion range
3. False positive responses: Other metal ions interfere by binding to the ligand site diminishing the concentration reading and misleading the analyst.

More importantly, as far as we aware, no selenium sensor exists or has been developed for real-time environmental monitoring, while those available for mercury ions are not *selective, sensitive, reliable, nor portable.* Clearly, new innovative approaches for metal/metalloid, real-time sensors are urgently needed by the environmental community.

Synthesis of Hg^{2+} and SeO_4^{3-} Monomer Complexes and Polymerization Studies to Create Templated Bulk Polymers.

Murray et al. have constructed both a lead (Pb^{2+}) electrode and a fiber optic device for real-time sensing of lead (Pb^{2+}) ions in the 1-5 parts per trillion (ppt) range with the 4-vinylbenzoic acid-Pb^{2+} complex.[3a] They have also environmetally tested the Pb^{2+} ion selective electrode device in rivers in Maryland. Thus, we wish to utilize this same approach for constructing electrode and fiber optic devices for mercury (Hg^{2+}) ion real-time sensors, so that we can test this device the first year for selectivity and analytical sensitivity at the sites of interest. Initial studies will include fluorescent spectral analysis of the 4-vinylbenzoic acid-Hg^{2+} complex, selectivity with other competing metal ions, and analytical sensitvity measurements (ppt range) to determine appropriate parameters for real-time analysis of Hg^{2+} ions at environmental sites of interest. Polymerization studies of the (4-vinylbenzoic acid)$_2$$Hg^{2+}$ complex, on an fiber optic or electrode surface will be followed by testing at environmental sites of interest.

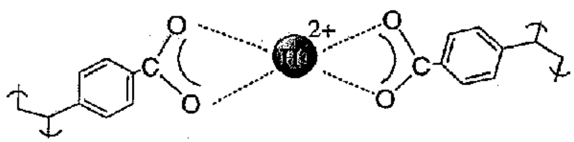


Figure 2: Mercury Selective, Templated Polymer for Reat-Time Detection

In another method, that may provide a more selective and sensitive Hg^{2+} ion sensor, the following templated Hg^{2+}-monomer complex will be synthesized by the reaction shown below and its' fluorescence spectral properties fully studied **(Figure 3)**. The two new approaches will be used to develop highly selective and sensitive sensors for both Hg^{2+} and SeO_4^{3-} ions. The first approach entails the photo-induced electron transfer technique (PET), where the non-metal containing monomer **(Figure 4)** *does not provide fluorescence* due to a quench of this optical phenomena via the non-bonding electrons of the nitrogen atoms, but the Hg^{2+} complex *does fluoresce* when the nitrogen atom non-bonding electrons are bound to Hg^{2+}; **Figure 5** shows the same process with the templated polymer. Thus, high Hg^{2+} ion selectivity to this system, already shown by Fish et al.[(2d)] for a somewhat similar non-fluorescent system, will expedite the Hg^{2+} ion optical sensor development; a similar approach can be accomplished for CH_3Hg^+ if there is interest from CALFED.

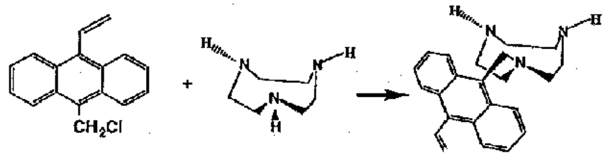


Figure 3: Synthesis of a Mercury Selective, Monomer Ligand, Non-Fluorescent by the PET process

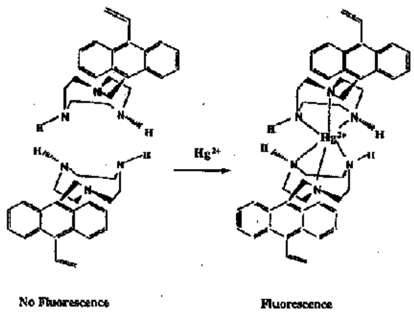


Figure 4: Synthesis of a Fluorescent, Monomer-Mercury Complex

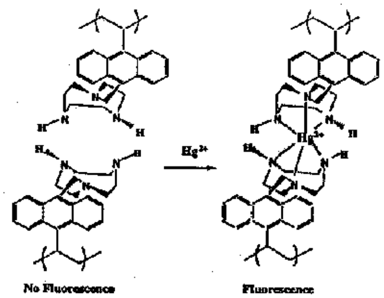


Figure 5: Demonstration of Quenched (PET) and the Enhanced Fluorescence Process with the Hg^{2+} Templated Polymer

The other technique for a SeO_4^{3-} sensor, used previously by Murray and co-workers for a Saran/Soman sensor (3a,b), utilizes a proposed europium ion-selenate complex that shifts the fluorescence spectrum to a unique wavelength for highly, selective selenate detection and quantitation (**Figure 6**). **Figure 7** clearly shows an example of a shifted fluorescence spectrum for selective lead ion (Pb^{2+}) detection at 544 nm.

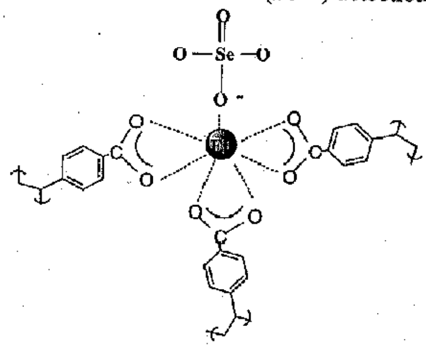


Figure 6: Europium-selenate polymer for selective SeO_4^{3-} detection via a fluorescent_wavelength shift

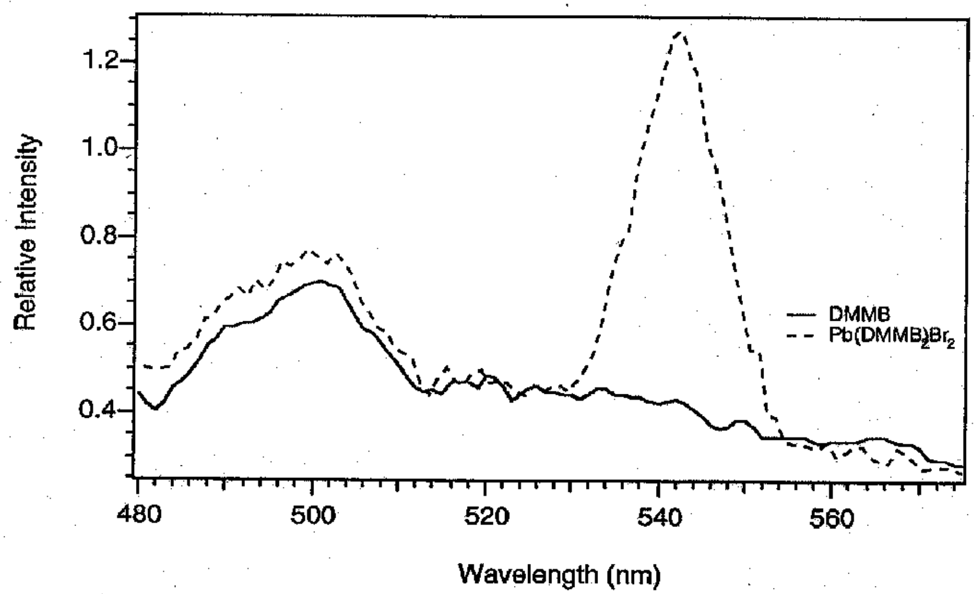


Figure 7. The spectra of the templated benzoic acid methyl ester ligand and its lead complex. Excitation with a 466.7 nm line of the argon-ion laser; detection of Pb^{2+} ions at ~ 544 nm.

Fabrication of Fiber Optic Sensors.

As an example of how we will generate a sensor device, these SeO_4^{3-} and Hg^{2+} monomer complexes can be bound by *in situ* co-polymerization to a 400 μm optical fiber surface. The luminescence spectrum of the polymer-coated optical fibers should show the same characteristic bands as the precursor templated SeO_4^{3-} and Hg^{2+} ion complexes. Prior to coating with the templated polymer, the fiber was washed with ethanol and distilled water. Varying amounts of the complex are then mixed with styrene, combined with a crosslinking agent divinylbenzene (DVB), and subjected to polymerization with constant mixing in the ultrasonicator. Azobisisobutyronitrile (AIBN) was used as an initiator in the amount of roughly 1 mole %. Polymerization will be carried out in a sealed vial with a inert (N_2) atmosphere to avoid the quenching of the free radicals by oxygen. Polymerization will be allowed to proceed until the content acquired a viscous/sticky consistency, at which moment the seal is broken and the optical fiber dip-coated with the polymer. Coated fibers will subsequently be cured overnight with UV light. The polymer coat is then swollen in the water/methanol solution and treated with EDTA or dilute acid to release the templates, SeO_4^{3-} or Hg^{2+}, coordinated by the polymerized ligands. The fluorometric probe will then be attached to the common trunk of the fiber. The polymer coated onto the tapered end of the fiber will be excited evanescently (light activated) and the resulting metal-ligand fluorescence will be collected into the same fiber, transmitted back to the bifurcation (fiber) and registered through the other leg using a portable fiber-optic spectrophotometer and portable lap-top computer (**Figure 8**).

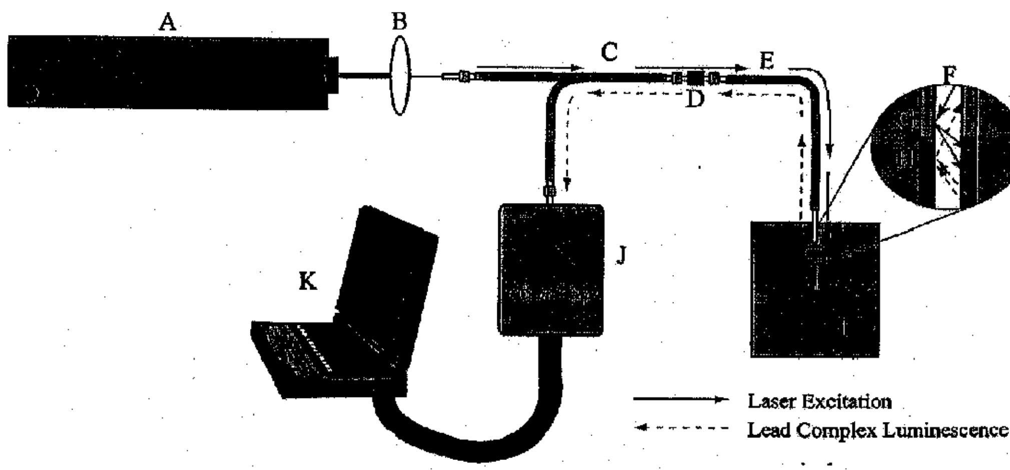


Figure 8. The experimental setup. *A* argon-ion laser, *B* focusing lens, *C* bifurcated fiber, *D* optical fiber coupler, *E* fiber optic probe, *F* fiber optic core, *G* original cladding, *H* templated polymer coating, *I* analyte solution, *J* fiber optic spectrophotometer, *K* detector; *L* A/D converter; *M* laptop computer.

Ecological/Biological Benefits

The primary stressor addressed by the program is contaminants entering the lower San Joaquin River and Cache Creek, which empties into the Sacramento River. The primary ecosystem and water quality benefits of sensor development are to: **(a)** allow real-time management of selenium discharges into the San Joaquin River and **(b)** allow improved management of mercury loads from mines in the Cache Creek watershed.

Secondary benefits from sensor development are a likely reduction in the number and/or magnitude of violations of the EPA selenium concentration objectives for the San Joaquin River downstream of the Merced River and of EPA mercury objectives in Cache Creek. Species and species groups benefiting from reduced selenium concentrations besides chinook salmon and steelhead trout, are delta smelt, longfin smelt, splittail, white and green sturgeon, striped bass, marine/estuarine fishes and large invertebrates, and Bay-Delta aquatic foodweb organisms.

During the final year of the research and development phase of the proposed project the research team will upgrade key real-time SJR water quality monitoring stations with the prototype selenium sensor devise and deploy the mercury sensor device at monitoring locations downstream from the most important mercury discharge or source points. This information provided by the final year deployment of the prototype sensor devices can be used to assess the impact of other management practices that attempt to reduce the toxic metal ion pollutant load into the lower SJR and Bay-Delta. Species and species groups benefiting from reductions in contaminants entering the Bay-Delta are delta smelt, longfin smelt, splittail, white and green sturgeon, striped bass, resident fish species, marine/estuarine fishes and large invertebrates, Bay-Delta aquatic foodweb organisms, and waterfowl.

Non-ecological CALFED objectives addressed by the program include improving Bay-Delta water quality for drinking water, industrial, and recreational beneficial uses. The program will facilitate the control and timing of agricultural and mining drainage to coincide with periods when dilution flow is sufficient to achieve CALFED water quality concentrations. The discharge into the SJR of agricultural drainage that is high in selenium is one of the most serious contaminant problem in the Bay-Delta. Selenium (selenate, SeO_4^{3-}) has caused reproductive failure in sensitive fish species and developmental deformities in waterfowl and shorebirds, because of its ability to bioaccumulate within food chains in plant and animal tissue to levels that can be toxic to higher trophic organisms. Finally, the program will be managed to dovetail with CALFED's Water Quality Program, the geographic scope of which is limited to the legally defined Delta.

Background and Biological/Technical Justification

Real-time management of west-side San Joaquin selenium drainage and management of Sacramento Basin mercury discharges are specified goals of the CALFED Water Quality Program. A demonstration of the capabilities and benefits of real-time salinity management by the SJRMPís Water Quality Subcommittee has received funding by CALFED. Salinity can be measured in real-time through the real-time forecasting of selenium water quality cannot be performed with the requisite degree of accuracy for compliance purposes without the deployment of a continuously recording selenium sensor device. In the Grassland Bypass Project neither electrical conductivity or flow are adequately correlated with selenium concentrations to be useful in selenium load forecasting. In the case of mercury mine discharge management from sources in Cache Creek, lack of a continuously recording mercury sensor compromises the development and implementation of the Total Mass Daily Load (TMDL) program actions, specified amongst the CALFED water quality actions. The project's primary benefit is to increase the frequency of meeting San Joaquin and Sacramento River water quality objectives for selenium and mercury ion concentrations.

Deployment of Real-Time Selenate and Mercuric Ion Sensors.

Real-time sensor devices for mercury (Hg^{2+}, sensitivity in the ppt range) and selenium (SeO_4^{3-}, sensitivity in the ppt range) ions will be installed at existing monitoring sites currently maintained by the CRWQCB, USGS, and local agencies. The sensor devices will be designed to give a 0-5V DC output so as to be compatible with current datalogging systems such as the Campbell CR-10 used by the USGS or the HANDAR 2000 used by the Department of Water Resources. The sensor devices can be used for long-term monitoring, but will need to be EDTA or acid washed to remove the just determined metal ion concentration after each experiment. This procedure can be easily and safely done on-site.

Location and/or Geographic Boundaries of Project

The geographic area encompassed by the program is the lower San Joaquin River basin, including west-side tributaries, in the following counties: Stanislaus, Merced, Modesto, San Joaquin, Tuolumne; and Cache Creek in Yolo County.

Justification for Project and Funding by CALFED

Real-time management of west-side San Joaquin selenium drainage, and management of Sacramento Basin mercury discharges are specified goals of the CALFED Water Quality Program. Real-time forecasting of selenium water quality cannot be performed with the requisite degree of accuracy for compliance purposes *without the deployment of a real-time, selective selenium (SeO_4^{3-}) and mercury (Hg^{2+}) ion sensors.* In the Grassland Bypass Project, neither electrical conductivity measurements nor flow measurements are adequately correlated with selenium (SeO_4^{3-}) concentrations to be useful in selenium load forecasting. In the case of mercury mine discharge management from sources in Cache Creek, lack of a real-time mercury (Hg^{2+}) ion sensor compromises the development and implementation of the Total Mass Daily Load (TMDL) program actions, specified amongst the CALFED water quality actions. The project's primary benefit is to increase the frequency of meeting San Joaquin and Sacramento River water quality objectives for selenium (SeO_4^{3-}) and mercury (Hg^{2+}) ion concentrations. More importantly, there are no available commercial real-time, selective sensors for either selenium (SeO_4^{3-}) or mercury (Hg^{2+}), and thus a global environmental need for these type of sensor devices would position the CALFED program as the leading agency in their development, fabrication, and deployment. Thus, these templated polymer sensors are: (1) Timely need for these devices; (2) more economical than sampling techniques and off-site analysis; (3) Action can taken immediately to address environmental problems; (4) acute toxicity events are known more quickly via logged concentrations of toxic metal ions at frequent intervals.

Monitoring and Data Evaluation

The monitoring data gathered during field deployment of the selenate and mercuic ion sensor devices will be compared to field data collected by the CRWQCB and other agencies at key monitoring locations. Data comparisons will be published, to encourage technology transfer for the new templated polymer sensor technology where appropriate.

Program Support and Compatibility with CALFED Objectives

The project is directly related to the recommended CALFED Water Quality Program actions to develop a real-time selenium water quality management system for the lower San Joaquin River, and to develop a TMDL for mercury load management to Cache Creek. The project goals have considerable support amongst the potential user community including the San Joaquin River Management Program (SJRMP), the California Regional Water Quality Control Board (CRWQCB-CVR), the United States Bureau of Reclamation and local San Joaquin basin and Sacramento basin stakeholders.

Participants/Collaborators in Implementation:

San Joaquin River Management Program (SJRMP); California Regional Water Quality Control Board, Central Valley Region (CRWQCB-CVR)

United States Bureau of Reclamation; Local SJR basin stakeholders (reservoir operators, water and drainage districts). The SJR Real Time Water Quality Monitoring Network Demonstration Project confirmed the technical feasibility of real time monitoring in the Lower SJR Basin. Successful implementation of this project will: Facilitate the control and timing of agricultural drainage to coincide with periods when dilution flow is sufficient to achieve CALFED water quality concentrations (CALFED Priority Action 1).

Support efforts of local watershed programs that improve water quality parameters of concern within the Delta tributary watersheds (CALFED Priority Action 21) by providing real time water quality data and forecasts to river stakeholders.

Scope and Tasks to Accomplish Project

The scope of work encompassed by sensor research and development implementation requires funding for the following tasks:

Task 1 Synthesis and characterization (^{1}H NMR, MS, Elemental analysis) of the monomer ligands, N-(9-vinylanthracenyl)TACN and 4-vinylbenzoic acid, and studies of their fluorescence spectra to ascertain a unique wavelength for each ligand or to observe a fluorescence quench known as the Photoinduced Electron Transfer Effect (6 months to 1 year at LBNL).

Task 2 Synthesis and characterization(NMR, MS, elemetal analysis) of the monomer N-(9-vinylanthracenyl)TACN-mercury (Hg^{2+}) and bis(4-vinylbenzoic acid)-Hg^{2+} monomer complexes and study of their fluorescence properties for specific wave-length determination for the sensor application. Synthesis and characterization of the monomer tris(4-vinylbenzoic acid)Eu-SeO_4^{3-} complex and study its' fluorescence properties for specific wave-length determination for the selenium sensor application (first year, LBNL/JH-APL).

Task 3 Bulk polymerization studies of the monomer N-(9-vinylanthracenyl)TACN-mercury (Hg^{2+}) and bis(4-vinylbenzoic acid)-Hg^{2+} complex, removal of the Hg^{2+} ion template with 6N hydrochloric acid treatment, and selectivity studies of the templated polymers with Hg^{2+} ions and other potential competing metal ions in the actual water samples that will be used for future real-time Hg^{2+} ion sensing. Similar studies with the monomer tris(4-vinylbenzoic acid)Eu-SeO_4^{3-} complex will also be accomplished using the same protocol as described for Hg^{2+} ions (end of first year and second year, LBNL/JH-APL).

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Task 4 Polymerization of the monomers N-(9-vinylanthracenyl)TACN-mercury (Hg^{2+}) complex, bis(4-vinylbenzoic acid)-Hg^{2+}, and the tris(4-vinylbenzoic acid)Eu-SeO_4^{3-} complex onto fiber optic and electrode probes for real-time sensors. Analytical data-selectivity (high for metal ion to be detected), and sensitivity parameters (ppt range) using the set-up described in Figure 8 (second year), JH-APL/LBNL).

Task 5 Field studies with the portable laptop computer and fiber optic/electrode probe for the accurate, selective measurements of both Hg^{2+} and SeO_4^{3-} ions at the enviromental sites of interest (first year [Hg^{2+}] sensor and second year [SeO_4^{3-}], LBNL/JH-APL).

See the Table below that we have constructed as the equivalent to the Hypothesis Testing Information for Real-time Sensor Development in a specific Task sequence. To reiterate, it is is essential that all tasks are funded, since each task is critical for the next task to be accomplished.

Real-time Sensor Development in Sequence

Sensor Objectives[a]			
Task 1	Synthesis of the monomer ligands selective for Hg^{2+} and SeO_4^{3-}	High selectivity to metal ion of choice is critical for sensor development	High Priority
Task 2	Synthesis of the monomer-Hg^{2+} and SeO_4^{3-} complex and fluorescence spectral analysis	Determination of the unique wave-length for specific detection of Hg^{2+} or SeO_4^{3-}	High Priority
Task 3	Bulk polymerization of Hg^{2+} and SeO_4^{3-}; selectivity with the demetallated polymer	Determination of the selectivity upon reintroduction of Hg or Se to the bulk polymer material	High Priority
Task 4	Polymerization of monomers to the fiber optic / electrode probes for sensitivity studies in the ppt range	Fabricate sensor device for testing for the ppt sensitivity limits	High Priority
Task 5	Field studies at the sites of interest described in the text	Testing portable unit for long-term monitoring studies	High Priority

[a]It should be clear that for each metal ion sensor, the Task sequence, 1-5, has to be followed. Thus, inorder to fabricate a real-time sensor, each Task must be accomplished in sequence.

Schedule Milestones

First year: Synthesis of Hg^{2+} and SeO_4^{3-} vinyl monomer complexes; selectivity to competing metal ions, sensitivity studies in the parts per trillion range (ppt), and polymerization studies. Start the fabrication of the devices, both optical and electrochemical for Hg^{2+} and/or SeO_4^{3-}, whichever is more important to the goals of CALFED.

Second Year: Fabrication of devices and testing the fiber optic and electrochemical sensors for analytical limits (parts per trillion), while initiating field tests.

07-Apr-99

Lawrence Berkeley National Laboratory
Real-Time Sensors for Mercuric and Selenate Ions Utilizing
Templated Polymer Technology
(Principal Investigator – R. Fish)

Table 3 – Total Budget

Task	Direct Labor Hours	Direct Salary and Benefits	Service Contracts	Materials and Acquisition Costs (inc. subcontract)	Miscellaneous and other Direct Costs	Overhead and Indirect Costs	Total Cost
Task 1	1089	43,493	0	41,834	19,083	30,548	134,958
Task 2	1089	40,935	0	39,374	17,960	28,751	127,019
Task 3	1299	48,610	0	46,756	21,328	34,142	150,835
Task 4	1089	40,935	0	39,374	17,960	28,751	127,019
Task 5	2178	81,869	0	78,747	35,920	57,502	254,039
Totals	6744	255,841	0	246,085	112,250	179,695	793,871

Materials and Acquisitions includes a two year subcontract to Johns Hopkins University, Applied Physics Laboratory for a total of $199,691 (separate budget attached).

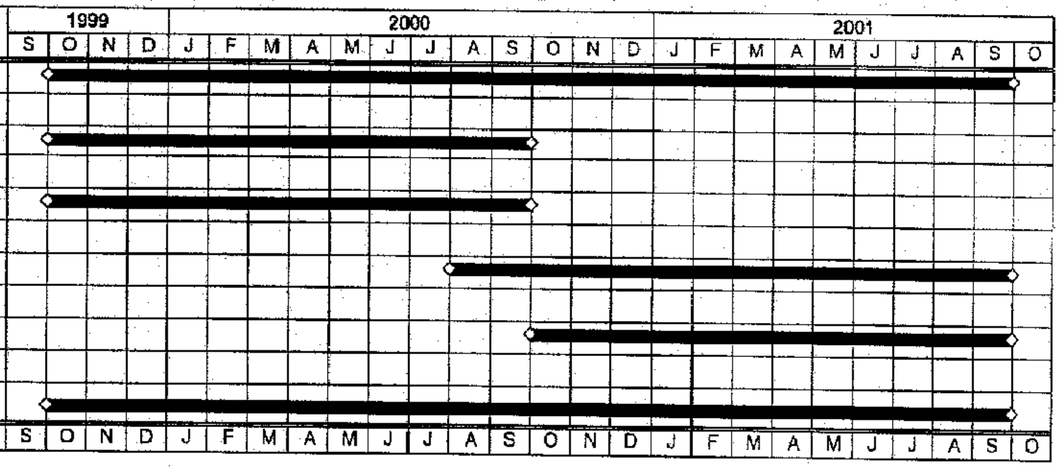
Lawrence Berkeley National Laboratory
Real-Time Sensors for Mercuric and Selenate Ions Utilizing
Templated Polymer Technology
(Principal Investigator - R. Fish)

Table 4 – Quarterly Budget

Task	Quarterly Budget Oct – Dec 99	Quarterly Budget Jan – Mar 00	Quarterly Budget Apr – Jun 00	Quarterly Budget Jul – Sep 00	Quarterly Budget Oct – Dec 00	Quarterly Budget Jan – Mar01	Quarterly Budget Apr – Jun 01	Quarterly Budget Jul – Sep 00	Total Budget
Task 1	20,000	30,000	30,000	34,000					114,000
Task 2	16,000	30,000	30,000	52,000					128,000
Task 3				33,000	34,000	33,000	34,100	24,050	158,150
Task 4					30,000	32,000	34,000	32,220	128,220
Task 5	15,000	25,000	45,000	45,000	45,000	45,000	25,000	20,501	265,501
Totals	51,000	85,000	105,000	164,000	109,000	110,000	93,100	76,771	793,871

Real-Time Sensors for Mercuric and Selenate Ions Utilizing Templated Polymer Technology

Activity Name	Start Date	Finish Date
Project Span	10/1/99	9/30/01
Task 1	10/1/99	9/30/00
Task 2	10/1/99	9/30/00
Task 3	8/1/00	9/30/01
Task 4	10/1/00	9/30/01
Task 5	10/1/99	9/30/01



THE JOHNS HOPKINS UNIVERSITY - APPLIED PHYSICS LABORATORY
COST SUMMARY REPORT
Project Summary by Year - Project Period of Performance = Oct 1999 to Sep 2001
(for all WBS IDs and Departments)

Page 1
07-Apr-1999

Project ID : RTIME | Proposal ID : | Proposal Title : | Task ID : | Cost Model : M6

	Total RTIME Staff Hours	Staff Months	Cost
Direct Labor Cost			
Principal			
Senior Upper	296.00	2.0	12,602
Senior Lower			
Associate	2,673.00	18.1	72,075
Technical			
Clerical			
Craft & Service			
Total Direct APL Labor	2,969	20.1	84,678
Employee Fringe			40,391
Direct RSE Labor			
Dept. Ovhd. on Dir. Labor			40,984
Sub-Total	2,969	20.1	166,053
Direct Procurement Cost			
Material			2,000
Subcontract			
Sub-Total			2,000
Procurement Burden			
Procurement Burden			85
Other Direct Cost			
RSE Non-Salary			
RSE ODC			
Travel			3,094
Consulting			
Special Test Equipment			
Miscellaneous Other Direct Cost			
Sub-Total			3,094
Total Direct Labor + Procurement Burden + ODC			169,232
Admin & Research Burden			26,400
Total Estimated Cost			197,632
Cost of Money			2,058
Total Estimated Cost + COM			199,690
Fee			
Total Est. Cost, Fee, COM	2,969	20.1	199,690

* Totals and sub-totals may not add due to rounding.

Use or disclosure of data contained on this sheet is subject to the restriction on the title page of this proposal.

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I-018637

I-018637

THE JOHNS HOPKINS UNIVERSITY - APPLIED PHYSICS LABORATORY
COST SUMMARY REPORT
Project Summary by Year - Project Period of Performance = Oct 1999 to Sep 2001
(for all WBS IDs and Departments)

Project ID : RTIME	Proposal ID : Proposal Title :	Task ID :	Cost Model : M6

	FY 2000				FY 2001				FY 2002			
	Rates	Staff Hours	Staff Months	Cost	Rates	Staff Hours	Staff Months	Cost	Rates	Staff Hours	Staff Months	Cost
Direct Labor Cost												
Principal												
Senior Upper	41.78	148.00	1.0	6,183	43.37	148.00	1.0	6,419				
Senior Lower												
Associate	26.47	1,365.00	9.2	36,132	27.48	1,308.00	8.8	35,944				
Technical												
Clerical												
Craft & Service												
Total Direct APL Labor		1,513	10.2	42,315		1,456	9.8	42,363				
Employee Fringe				20,184				20,207				
Direct RSE Labor												
Dept. Ovhd. on Dir. Labor				20,480				20,503				
Sub-Total		1,513	10.2	82,980		1,456	9.8	83,073				
Direct Procurement Cost												
Material				1,000				1,000				
Subcontract												
Sub-Total				1,000				1,000				
Procurement Burden												
Procurement Burden				42				43				
Other Direct Cost												
RSE Non-Salary												
RSE ODC												
Travel				1,547				1,547				
Consulting												
Special Test Equipment												
Miscellaneous Other Direct Cost												
Sub-Total				1,547				1,547				
Total Direct Labor + Procurement Burden + ODC				84,569				84,663				
Admin & Research Burden				13,193				13,207				
Total Estimated Cost				98,761				98,870				
Cost of Money				1,011				1,047				
Total Estimated Cost + COM				99,773				99,918				
Fee												
Total Est. Cost, Fee, COM		1,513	10.2	99,773		1,456	9.8	99,918				

* Totals and sub-totals may not add due to rounding.

Use or disclosure of data contained on this sheet is subject to the restriction on the title page of this proposal.

Applicant Qualifications:

Richard H. Fish, PhD. (Staff Scientist/Chemist, Lawrence Berkeley National Laboratory). Dr. Fish received a BS in Chemistry from the University of Rhode Island in 1961 and a PhD in organic/organometallic chemistry in 1964. His primary research interest the last 6 years at LBNL has been in the environmental separation sciences field and focused on the synthesis of designer polymer pendant ligands/templated polymers for selective metal ion removal from waste waters. He is the author of over 125 publications, patents, book chapters, and reviews on organic, organometallic, and environmental chemistry topics. Previous support of the imprinted polymer chemistry, FY 1993-FY 1997, by the U. S. Department of Energy, Office of Environmental Management.

George M. Murray, PhD (Staff Scientist/Chemist, John Hopkins University, Applied Physics Laboratory). Dr. Murray received a BS in Chemistry from the University of Tennessee in 1982 and a PhD in Analytical Chemistry in 1988 from the same institution. His primary research interests the last 5 years has been in the templated polymer field and focused on the synthesis of designer templated polymers for selective metal ion sensors and the fabrication of sensor devices, using both optical and electrochemical detection. He is the author of over 50 publications, patents, book chapters, and reviews on environmental and analytical chemistry topics. Imprinted polymer chemistry support , FY 1997-FY 1999, by the U. S. Department of Energy, Office of Environmental Management.

Nigel Quinn PhD, P.E. (Geological Scientist, Lawrence Berkeley National Laboratory) Dr. Quinn received a BSc (Hons) in irrigation engineering and hydrology from the Cranfield Institute of Technology in England, an MS in Agricultural and Civil Engineering from Iowa State University and a PhD in civil and environmental engineering from Cornell University in 1987. His primary research interests have centered on the development of real-time forecasting tools for the San Joaquin River and selenium fate and transport modeling. He is the author of over 50 publications and reports on various aspects of water resources and drainage engineering.

References Cited

[1] San Joaquin River Management Program Water Quality Subcommittee. **1997**. Demonstration of the San Joaquin River Real Time Water Quality Monitoring Network. DWR San Joaquin District Office Report to the United States Bureau of Reclamation. In progress.

[2] (a) Chen, H.; Olmstead, M. M.; Albright, R. L.; Devenyi, J.; Fish, R. H. *Angew. Chem. Int. Ed. Engl.* **1997**,*36*, 642 and references therein. (b) Fish, R. H. Metal Ion

Templated Polymers. Studies of N-(4-Vinylbenzyl)-1,4,7-Triazacyclononane-Metal Ion Complexes and their Polymerization with Divinylbenzene: The Importance of Thermodynamic and Imprinting Parameters in Metal Ion Selectivity Studies of the Demetalated Templated Polymers. ACS Symposium Series 703. *Recognition with Imprinted Polymers.*, **1998**, P238. (c) Murray, G. M.; Fish, R. H. Chemical Slippers. *New Scientist*, **September 13, 1997**, P34. (d) H. C. Lo, H. Chen, R. H. Fish Metal-Ion Templated Polymers. Synthesis of an {[mono-N-(4-Vinylbenzyl)-1,4,7-Triazacyclononane]$_2$Hg}(OTf)$_2$ Sandwich Complex, Polymerization of this Monomer with Divinylbenzene, and Hg^{2+} Ion Selectivity Studies with the Demetallated Resin. *Chem. Commun.* **1999**, in press.

[3] (a) Murray, G. M. et al. Templated Polymers for the Selective Sequestering and Sensing of Metal Ions. ACS Symposium Series 703. *Recognition with Imprinted Polymers.*, **1998**, p218. (b) Murray, G. M. et al. Molecularly Imprinted Polymers for the Selective Sequestering and Sensing of Metal Ions. *John Hopkins APL Technical Digest* **1997**, *18*,464. (c) Jenkins, A. L.; Uy, O. M.; Murray, G. M. Polymer-Based Lanthanide Luminescent Sensor for Detection of the Hydrolysis Product of the Nerve Agent Soman in Water. *Anal. Chem.* **1999**, 71, 373.

Attachments

Letters of Support

Letter to Merced County Board of Supervisors.

Geographic map of areas of interest

I-018640

SUMMERS ENGINEERING, INC.
CONSULTING ENGINEERS
887 N. IRWIN ST. · P. O. BOX 1122
HANFORD, CALIFORNIA 93232

JOSEPH B. SUMMERS
JOSEPH C. McGAHAN
ROGER L. REYNOLDS
BRIAN J. SKAGGS
SCOTT L. JACOBSON

Note new area code →
TELEPHONE (559) 582-9237
TELECOPIER (559) 582-7632

April 13, 1999

COPY

Dr. Dick Fish
LAWRENCE BERKELEY NATIONAL LABORATORY
1 Cyclotron Road, 70-215A
Berkeley, CA 94720

SUBJECT: Grassland Area Farmers Support for CALFED Grant Proposals.

Dear Dr. Fish:

The Grassland Area Farmers have a long history of supporting innovative drainage reduction strategies on the west side of the San Joaquin Valley. As the proponent of the Grassland Bypass Project, the Grassland Area Farmers have invested millions of dollars in the past 3 years to improve monitoring and increase control over subsurface tile drainage leaving the area. Significant reductions in selenium loads contained in these discharges have been necessary to meet the strict selenium load limits imposed by the Project.

The CALFED proposal entitled "Real-Time Sensors for Selenate and Mercuric Ions Utilizing Templated Polymer Technology" is of great interest to the Grassland Area Farmers. The Grassland Area Farmers spend tens of thousands of dollars each year on selenium analyses to monitor discharge within the drainage area to meet monthly selenium load targets. The most troubling aspect of these analyses is the time it takes to obtain a result – often a week or more. A real-time selenium sensor that could provide information to our existing telemetered monitoring system could not only save the Grassland Area Farmers money but also provide more timely information.

Sincerely,

Joseph C. McGahan
Drainage Coordinator for Grassland Area Farmers

JCM/p

PANOCHE WATER DISTRICT

52027 WEST ALTHEA, FIREBAUGH, CA 93622 • TELEPHONE (209) 364-6136 • FAX (209) 364-6122

April 12, 1999

Dr. Dick Fish
Lawrence Berkeley National Laboratory
1 Cyclotron Road, 70-215A
Berkeley, CA 94720

Subject: Panoche Water District Support for CALFED Grant Proposals

Dear Dr. Fish:

The Panoche Water District has a long history of supporting innovative drainage reduction strategies on the west-side of the San Joaquin Valley. As a participant in the Grassland Bypass Project the water district has invested millions of dollars in the past 3 years to improve monitoring and increase control over subsurface tile drainage leaving the water district. Significant reductions in selenium loads contained in these discharges have been necessary to meet the strict selenium load limits imposed by the Project.

The CALFED proposal entitled "Real Time Sensors for Selenate and Mercuric Ions Utilizing Templated Polymer Technology" is of great interest to the District. The District spends tens of thousands of dollars each year on selenium analysis to monitor individual sumps within the District and to help meet monthly selenium load targets. The most troubling aspect of this analysis is the time it takes to obtain a result – often a week or more. A real-time selenium sensor that could be hooked up to our existing telemetered monitoring system could not only save the District money but also provide more timely information.

Sincerely,

Dennis Falaschi
General Manager

Lawrence Berkeley Laboratory
1 Cyclotron Road Berkeley, California 94720
(510) 486-4000

NIGEL W.T. QUINN, PhD, P.E
EARTH SCIENCES DIVISION
PHONE: (510) 486 7056 FAX: (510) 486 7152

March 30, 1999.

Ms. Lydia Beiswanger, Chief Deputy
Merced County Board of Supervisors
2222 M Street
Merced, CA 95340.

Dear Ms. Beiswanger;

This letter is to inform you of our intent to submit a proposal to the CALFED Bay-Delta Program entitled "Real-Time Sensors for Selenate and Mercuric Ions Utilizing Templated Polymer Technology". If successful in our application we intend to test this sensor at sites within the Grasslands Drainage Basin and at gauging stations such as Crows Landing along the San Joaquin River.

Agricultural and wetland water districts within the county spend tens of thousands of dollars each year on selenium analysis to monitor supply water and drainage return flows. The most troubling aspect of this analysis is the time it takes to obtain a result -- often a week or more. A real-time selenium sensor that could be hooked up our existing telemetered monitoring system could not only save these water districts money but also provide more timely information.

Likewise, in the both the San Joaquin Valley and Sacramento Valley, mercury associated with sediments from mine sites, mobilized by rainfall-runoff events creates hazards to the riverine ecosystem. A real-time mercury sensor would help to provide quantification and early warning of these hazards.

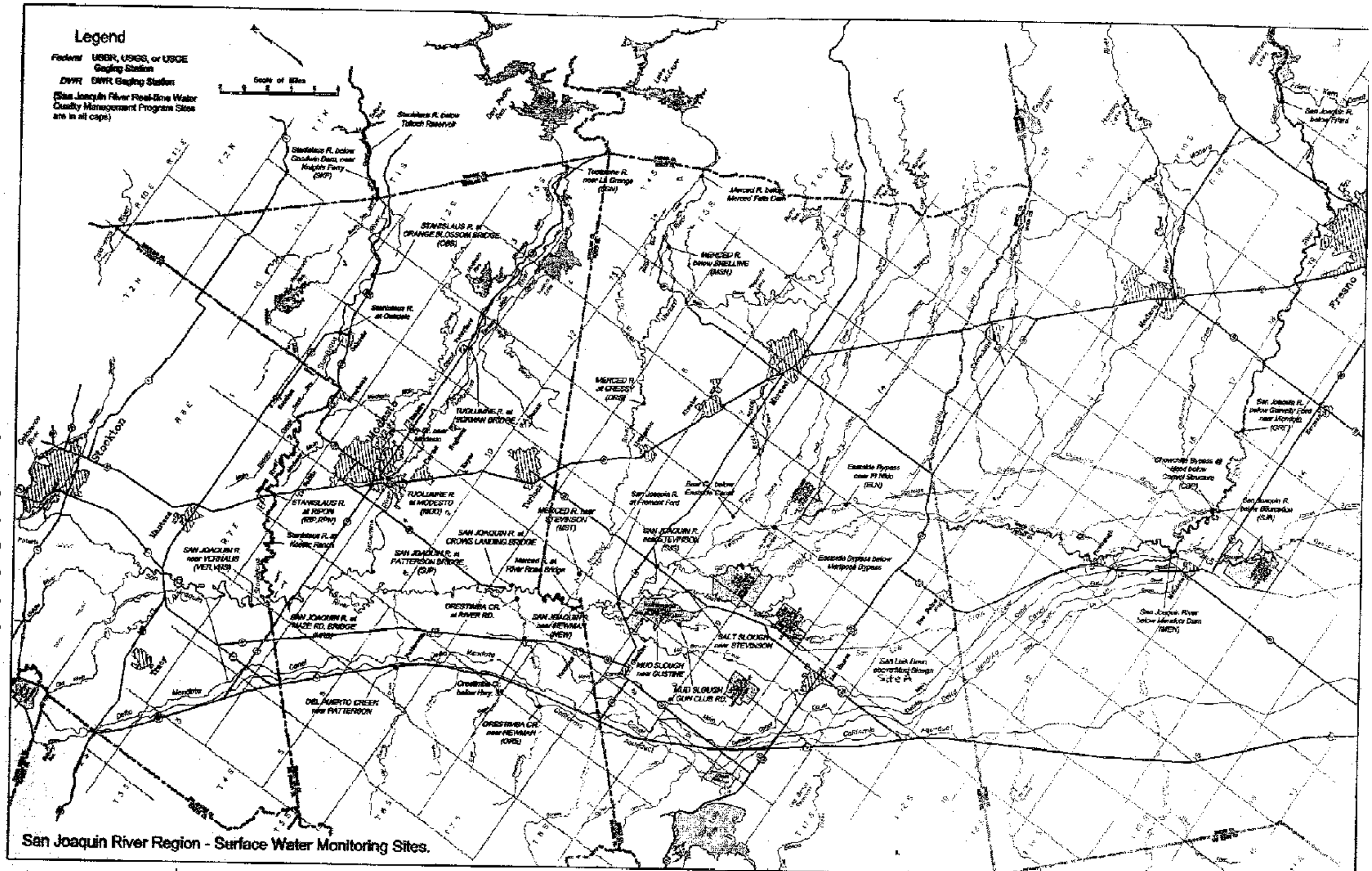
We anticipate considerable interest in the successful development and deployment of these sensors by water districts and wetland managers in Merced County.

Sincerely,

Nigel W.T. Quinn

Nigel W.T. Quinn

Geological Scientist



San Joaquin River Region - Surface Water Monitoring Sites.

12/11/98