Effectiveness Monitoring Committee

Full Project Proposal Form

Deadline for Submission: To Be Included In
Invitation for Full Proposal

Project #: EMC2021-001 **Date:** 12/01/2021

Project Title: Aquatic Toxicity and Cumulative Watershed Effects of Pesticide Discharge Related to Post-Fire Reforestation

Principal Investigator(s): REDACTED

Collaborators: Central Valley Regional Water Quality Control Board, USGS California Water Science Center

Contact Information: REDACTED

[redacted] **(Years/Months):** 3/0

Written Proposal Requirements:

Please address each of the following for consideration by the EMC. For further information please see the Request for Proposals or consult section 5.0 of the EMC's Strategic Plan.

1. **Background and Justification**
2. **Objectives and Scope**
3. **Critical Questions and Forest Practice Regulations Addressed**
   Please identify the Critical Questions by number and letter (as identified in the EMC's strategic plan), and the associated regulations by number. Please also describe how your project will address these questions and the efficacy of each regulation.
4. **Research Methods**
5. **Scientific Uncertainty and Geographic Application**
   Please consult section 4.4 of the EMC's strategic plan for further information.
6. **Collaborations and Project Feasibility**
7. **Project Deliverables**
8. **Detailed Project Timeline**
9. **Requested Funding**
   Please provide the total requested amount of funding along with a line item budget for each fiscal year of the project (see page 2).

Include figures, tables, or photos as needed.

Please ensure that all "Categories" below are addressed in your budget. This will ensure that all information required by the state contracting process is present. You may break each "Category" into as many sub-categories as needed to fully describe your budget.

Category	Description	Year 1	Year 2	Year 3	Total
Personnel *Identify all personnel costs including field technicians, graduate students, Principal Investigators, etc.* ***Show these values as individual rates per unit of time.***					
Fringe Benefits *Cite as actual benefits or a percentage of personnel costs.*					
Other					
Operating Expenses *Include rent, supplies, and equipment costs as separate line items*					
Indirect Cost *Not to exceed 15%*					
Travel *Express as per diem rates specified by CalHR, or verification that such rates are not available to you.*					
Total Cost					
Matching or In-Kind Contributions					
EMC Funding Requested					

Responses to concerns raised in the concept proposal acceptance letter can be found in the following sections:

Describe grab, active, and passive sampling methods in more detail;
Pages 5-6

Provide information on study site location(s), and the forest district(s) that apply to the study's scope, and describe potential for broader applicability of the geographic scope of the study to forested ecosystems in California where the California Forest Practice Rules (FPRs) apply;
Page 9

Clearly articulate the research questions and how they relate to the specific California Forest Practice Rules being tested. Include any validation plans associated with this study;
Pages 4 and 5, appendix section A1

Clarify the difference between use of "pesticides" and "herbicides," if any, in the context of the study methods; and
Page 2, paragraph 1

Describe prior collaborative work as briefly mentioned in the Initial Concept Proposal, how it relates to the proposed research, and if new or future collaborations will relate to or broaden the applicability of the current research.
Page 2, paragraph 3 and page 11, paragraph 1

Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

Aquatic Toxicity and Cumulative Watershed Effects of Pesticide Discharge Related to Post-Fire Reforestation

1. Background and Justification

According to Cal Fire's list of the Top 20 Largest Wildfires, published on October 25th, 2021, eight of the state's ten largest fires on record and twelve of the top twenty have happened within the past five years (California Department of Forestry and Fire Protection, 2021). The recent surge in catastrophic wildfires has increased forest regeneration efforts as well, and the use of herbicides (a type of pesticide) to ensure seedling survival has increased at a similar scale. Other pesticides such as insecticides or fungicides can be used for pests as well, but herbicides are the predominant type of pesticide associated with forestry, including controlling undesirable vegetation during reforestation.

To begin evaluating the potential impacts of herbicides used in a post-fire environment, the Central Valley Water Boards Forest Activities Program partnered with California Department of Fish and Wildlife's (CDFW) Water Pollution Control Laboratory in 2013 to begin active and passive sampling in the Battle Creek Watershed for herbicides used following the Ponderosa Fire. This initial collaboration focused on determining if passive and active samplers were capable of capturing pesticides used in post-fire regeneration. Twenty-six samples were collected during this first sampling event and the herbicide hexazinone was detected most frequently. Due to the large scale of the watershed, the detections could not be traced back to a direct source; however, this preliminary study provided the justification to continue evaluating the potential impacts of pesticides used in a post-fire environment.

The Forest Activities Program then began a multi-year partnership with the U.S. Geological Survey (USGS) Organic Chemistry Research Laboratory (OCRL). This partnership focused on developing a sampling methodology using Chemcatcher® passive samplers and refining analysis methods able to detect 155 pesticides in exposed passive sampler disks This sampling and analysis methodology were then used to sample eight sites in the Sierra Nevada foothills region during three storm runoff and two base flow sampling events in 2018 and 2019. A total of 22 pesticides, including 9 insecticides, 7 fungicides, and 6 herbicides, were detected in extracts from the passive samplers (Uychutin et al. 2021).

The Central Valley Regional Water Quality Control Board's (CVRWQCB) General Order for timberland management activities was modified in 2017 to require dischargers to comply with pesticide no-spray buffers, based on the preliminary data from these studies and other supporting material regarding the application of pesticides in a post-fire environment (CVRWQCB 2017). Buffers for Class I, II, III and IV watercourses are equal to the Watercourse and Lake Protection Zone (WLPZ) widths specified in the California Code of Regulations, title 14, section 936.5 when applying pesticides following post-fire salvage operations.

The Forest Activities Program has continued to test the efficacy of both active and passive samplers for the purpose of surface water screening and monitoring of pesticides used in commercial forestry and General Order permit compliance. In the winter of 2020/2021, Forest Activities Program staff deployed active and passive samplers in six locations within the North Salt Creek Watershed, a tributary to the northern Sacramento River. Portions of the North Salt Creek Watershed were affected by the Carr and Hirz fire in 2018. The herbicide hexazinone was detected at 5 of the 6 locations. Forest Activities staff continued to deploy samplers in post-fire environments in the 2021 summer months. Passive samplers were deployed in two Northern California watercourses located downstream of regeneration or timber salvage operations. The sampling events conducted in the 2021 summer months have all resulted in detections of hexazinone.

The provisions within the Central Valley Regional Water Quality Control Board's General Order go beyond those currently required under the FPRs or enacted by the California Department of Pesticide Regulation aimed to protect waters of the state from problems related to pesticide applications in forestry operations in post-fire environments. There are currently no requirements in the FPRs to address increased pesticide use following post-fire salvage logging on Substantially Damaged Timber Harvest Plans and Emergency Notices. FPRs provide minimal guidance directed toward mitigating the potential impacts from direct application or run-off from pesticide treatments in post-fire environments. The current lack of specific post-fire pesticide-related regulations in the FPRs has the potential to impact salmonid spawning and rearing habitats (916.4 & 916.9) or result in cumulative watershed effects in post-fire environments (916.9(b), Technical Rule Addendum (TRA) #2. It is not clear if the current regulatory framework or implemented mitigations adequately protect the beneficial uses of waters of the state when applied over large, burned areas.

14 CCR 896 of the FPRs states the purpose of the Forest Practice Rules is to implement the provisions of the Z'berg-Nejedly Forest Practice Act of 1973 in a manner consistent with other laws, including but not limited to, the Timberland Productivity Act of 1982, the California Environmental Quality Act (CEQA) of 1970, the Porter Cologne Water Quality Act, and the California Endangered Species Act. § 13240 of the Porter Cologne Water Quality Act gives each regional board the authority to formulate and adopt water quality control plans for all areas within the region. The Water Quality Control Plan (Basin Plan) for the CVRWQCB for the Sacramento River Basin and San Joaquin River Basin states "When a pesticide is detected more than once in surface waters, investigations will be conducted to identify sources. Priority for investigation will be determined through consideration of the following factors: toxicity of the compound, use patterns and the number of detections. These investigations may be limited to specific watersheds where the pesticide is heavily used, or local practices result in unusually high discharges. Special studies will also be conducted to determine pesticide content of sediment and aquatic life when conditions warrant. Other agencies will be consulted regarding prioritization of monitoring projects, protocol, and interpretation of results." The following proposed study directly aligns with the Basin Plan Objectives and therefore the general intent of the Forest Practice Rules.

One-liter grab sampling is currently an established method for determining the concentrations of pesticides in surface waters. However, the discrete timing of the grab sample does not capture longer-duration pesticide concentration dynamics that arise following episodic storms or pesticide applications. To assess cumulative watershed effects and potential toxicity, it is imperative to capture episodic events to determine if there are periods of exposure potentially impacting the function of the WLPZ and their ability to support and provide spawning and rearing habitat for salmonids. Passive sampling and active sampling are two evolving methodologies that can mitigate some of the limitations of 1-liter grab sampling. Currently there is not a clear understanding of the relation between passive, active and grab sampling detections and how the detections using the active and passive samplers relate to the established regulatory thresholds.

2. Objectives and Scope

This study will be a continuation of previous collaborative work by the CVRWQCB, CDFW and USGS to assess cumulative watershed effects, WLPZ function, and efficacy of the FPRs regarding commonly used herbicides applied in post-fire environments. The two objectives of this project are: 1) compare passive, active, and traditional grab sampling techniques to assess strengths and weaknesses such as cost effectiveness, ability to sample episodic events, and ease of deployment and 2) Compare data from passive and active sampling to grab sampling to better understand the concentration results and how those may relate to regulatory thresholds. EMC funding will primarily be used for sample preparation and analyses, with matching funds from the USGS and CVRWQCB covering costs associated with field work, report writing and outreach efforts.

Sampling for the proposed study would occur between summer 2022 and summer 2023 with sample analysis complete by the end of the 2023 calendar year and a draft report to be completed by the end of the 2024 calendar year. Samples will be collected over three time periods, at three sites, for a total of nine sample sets. Sampling will occur in watersheds exposed to recent wildfire and where herbicide applications have occurred or are planned to occur. Pesticides to be analyzed will include the following 10 herbicides commonly used in forestry operations: aminopyralid, clopyralid, glyphosate, hexazinone, imazapyr, oxyfluorfen, penoxsulam, triclopyr, and 2,4-D (2,4-dichlorophenoxyacetic acid). Depending upon the availability of appropriate SPE disks, all sampling methodologies may not include the complete compound list. Pesticide detections and concentrations will be compared to pesticide use data and toxicity benchmarks where applicable. Field sampling will be conducted by staff from the USGS and the CVRWQCB. Sample analysis will be performed at the USGS OCRL in Sacramento, California.

3. Critical Questions and Forest Practice Regulations Addressed

This section describes how this proposal relates to the applicable rules, policies, and regulations of the Forest Practice Rules. Applicable critical questions, themes, FPRs, and policies are listed in appendix section A1.

There are very few specific rules addressing herbicide use in reforestation activities in the FPRs, and there are no specific rules addressing herbicide use in post-fire environments. However, a basic purpose of the FPRs is, among several other objectives, to protect the beneficial uses of water in accordance with the Porter-Cologne Water quality Control Act (14 CCR § 896 (a)) and any applicable Regional Water Quality Control Plan (14 CCR § 898.2 (h)).

The EMC Strategic Plan (2018) does not include critical monitoring questions related to post-fire water quality effects regarding herbicide uses, however it does recognize the need for additional methods for water quality monitoring of management practices in wildfire-affected areas (EMC Strategic Plan (2018), Appendix C).

The water quality concerns related to herbicide use in reforestation pertain to potential impacts on aquatic habitat, specifically the biologic and ecologic functions of stream and riparian habitats in managed timberlands; see EMC Theme #1 WLPZ Riparian Function. These habitats include communities of benthic organisms (including macroinvertebrates, algae, and microorganisms), amphibians, fish (spawning and rearing habitats), and presumably microorganisms within the sediments of the hyporheic zone (riparian groundwater); see Theme #5 Fish Habitat. Theme #2 Watercourse Channel Sediment may also apply, as herbicide use can affect the amount of protective vegetative ground cover and impact sediment delivery from steeper slopes. These water quality concerns also relate to 14 CCR § 916.3: General Limitations Near Watercourses, Lakes, Marshes, Meadows and Other Wet Areas.

This study addresses EMC Critical Question 5 (b) as statewide policies regarding post-fire herbicide use, which is applicable to watersheds that receive Anadromous Salmonid Protections (ASP), as well as those that do not (non-ASP). Samples may be collected from non-ASP watersheds, however the information gained relating to the aquatic transport and fate of these chemicals and sampling methodology will apply to both ASP and non-ASP watersheds. This also relates to FPRs in 14 CCR § 916.9, Protection and Restoration of the Beneficial Functions of the Riparian Zone in Watersheds with Listed Anadromous Salmonids.

The effects from large-scale herbicide applications in post-fire environments will likely arise from a combination of multiple projects consisting of Emergency Notices and substantially damaged Timber Harvesting Plans (THPs). This relates to cumulative impact assessments described in Technical Rule Addendum #2: Cumulative Impacts Assessment where it suggests such assessments include measurements to assess potential adverse effects and comply with an approved Water Quality Control Plan. Subsection (d) further indicates specific attention should be given to chemical contamination effects, which include direct application or run-off from pesticide treatments.

4. Research Methods

Three post-fire watersheds will be used as test regions for the sampling technique comparisons. These regions have been selected to include streams with a range of watershed characteristics and with consideration for accessibility and logistics. Four sampling devices or techniques will be used to measure the presence or concentration of herbicides in streams. All sample extracts will be analyzed by liquid chromatography with tandem mass spectrometry (LC-MS/MS) at the USGS OCRL. A brief description of each sampling technique is listed below with additional detail provided in appendix section A2.

Chemcatcher® Passive Sampler

Chemcatcher® passive samplers can be used for a variety of contaminants in surface water, including herbicides. Briefly, the Chemcatcher® passive sampler device functions by allowing target compounds in water to pass through an optional diffusion limiting membrane and accumulate in a solid phase extraction (SPE) disk (Kingston et al., 2006). The Chemcatcher® passive samplers can be deployed in streams for days to weeks which means that these passive samplers can capture episodic contaminant pulses without high-frequency field work. Analysis of the Chemcatcher® passive sampler extracts will provide an herbicide concentration in micrograms per disk which can provide valuable information about the presence or absence of herbicides, but it is difficult to relate Chemcatcher® results to aquatic life benchmarks. Results can however provide insight on relative abundance between sites and sampling periods.

Continuous Low-Level Aquatic Monitoring Active Sampler

The Continuous Low-Level Aquatic Monitoring device (CLAM) is an active sampler that can be deployed in streams for up to 48 hours at a time. The CLAM is a battery powered device that pumps water through an SPE disk similar to those used in the Chemcatcher® passive sampler, but the volume of water that is pumped through the CLAM is measured and recorded. The sample volume measurement allows for the calculation of herbicide concentrations in micrograms per liter. Results can be directly compared to aquatic life benchmarks and provide continuous monitoring that can capture episodic contaminant pulses. The primary drawbacks of the CLAM are the high cost (roughly $8,500/device), only one SPE disk will be used per CLAM deployment, and the limited number of SPE sorbents available in CLAM-compatible disks.

Solid Phase Extraction Robot Active Sampler

The Solid Phase Extraction robot (SPEbot) is an active water sampler that is currently being developed by the USGS. It is a low cost ($100-$700), user-assembled active sampler that pumps water through an SPE disk and measures the volume of water pumped through the device. The pumping regime is fully programmable, allowing for effectively continuous flow (the device pumps water in small pulses at a frequency of approximately 0.5 hertz) or multiple, discrete pumping intervals to create a composite sample and is therefore flexible relative to the needs of the sampling objectives. It can be deployed for approximately one week at a time and it can be configured with the same SPE disks that are used in the Chemcatcher® passive samplers. Like the CLAM, samples collected by SPEbot can be quantitated in micrograms per liter allowing for direct comparison to aquatic life benchmarks.

Discrete Surface Water Samples

Grab samples are collected to measure herbicide concentrations at a single point in time. A pre-cleaned 1-liter glass bottle will be submerged near the center of flow in a stream then sent to the analyzing laboratory for processing and analysis. Grab samples are collected according to the National Field Manual for the Collection of Water Quality Data (U.S. Geological Survey, 2006). The grab sampling method provides an herbicide concentration in micrograms per liter that can be directly related to aquatic life benchmarks. The primary drawbacks of grab sampling are the high labor costs associated with high frequency sampling plans and the potential to miss pulses of contaminants that might occur in between sampling trips.

Comparison Study Design

The four sampling methodologies will be compared in a series of three sampling events at three sites for a total of nine comparison tests. The testing schedule is designed to maximize the effectiveness of each sampling technique while minimizing field and analytical costs. The framework of the comparison study is adapted from a prior comparison study (Coes et al., 2014). Each comparison test event will last approximately 96 hours with a Chemcatcher® passive sampler and SPEbot deployed for the entire 96-hour interval, one CLAM deployed for hours 0 – 48, and a second CLAM deployed for hours 48– 96, and grab samples collected at hours 0, 48, and 96 (fig. 1). The three sampling events will be scheduled to target a spring storm event, summer baseflow conditions, and a late fall/early winter "first flush" storm event. The exact location and timing of sampler deployments will be based on pesticide-use notices submitted by private timberland owners to the California Department of Pesticide Regulation.

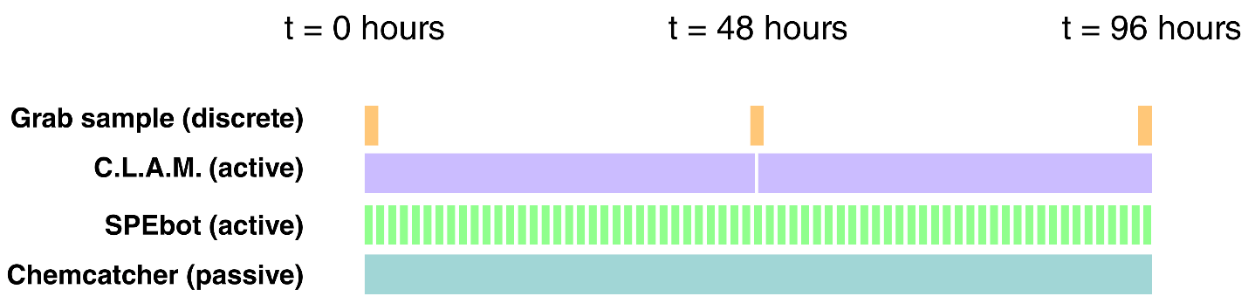

Figure 1. Event schedule of sampling techniques to be tested during the proposed project.

To address the comparison study objective, results from the comparison tests will be summarized and analyzed to assess the relative strengths and weaknesses of each sampling technique. Analytical results, cost, and ease of use will be considered in the assessment. To address the effectiveness of current FPRs with respect to protecting watersheds from potentially harmful herbicides, results will be compared to Environmental Protection Agency Office of Pesticide Programs Aquatic Life Benchmarks (EPA OPP; U.S. Environmental Protection Agency, 2020) or criteria described in the Water Quality Control Plan for the Central Valley Region (California Regional Water Quality Control Board Central Valley Region, 2018). Quality assurance and quality control samples (blanks, replicates, and matrix spikes) will be collected to validate results generated during the proposed study.

Analytical Methods

Three SPE sorbent types will be required to analyze for the 10 target compounds selected for this proposal (table 1). The Chemcatcher®, SPEbot, and surface-water grab samples can be configured with SPE sorbents that can accumulate all ten compounds; the CLAM can only be equipped with an SPE sorbent that can accumulate four of the ten target compounds. It may be possible to custom order disks for the CLAM that would allow for the analysis of all 10 compounds, but custom disk availability cannot be guaranteed. Delivery of results for all 10 compounds will depend on SPE sorbent availability for the different sampling techniques.

All samples will be analyzed at the USGS OCRL in Sacramento for up to 10 herbicides using methods described in Gross et al. (2021) and in documentation from the SPE disk manufacturer (Affinisep, 2021). Instrumental analysis will be performed using an Agilent 1260 high-performance liquid chromatography instrument coupled to a 6430 tandem mass spectrometry system (LC-MS/MS). Data quality will be ensured through the use of surrogate solutions containing isotopically labeled compounds to track losses during sample handling, an eight-point calibration curve with a minimum correlation coefficient of 0.99, instrument blanks, and calibration verification samples. After quantification, results are to be reviewed and uploaded into the OCRL Laboratory Information Management System before being released to the public in a USGS online data release and through the California Environmental Data Exchange Network (CEDEN).

Compound	Sorbent type	Grab	CLAM	CC	SPEbot
Hexazinone	SDB-RPS or HLB	✓	✓	✓	✓
Oxyfluorfen	SDB-RPS or HLB	✓	✓	✓	✓
Penoxsulam	SDB-RPS or HLB	✓	✓	✓	✓
Indaziflam	SDB-RPS or HLB	✓	✓	✓	✓
2,4 D	Anion exchange-SR	✓	*	✓	✓
Imazapyr	Anion exchange-SR	✓	*	✓	✓
Triclopyr	Anion exchange-SR	✓	*	✓	✓
Clopyralid	Anion exchange-SR	✓	*	✓	✓
Aminopyralid	Anion exchange-SR	✓	*	✓	✓
Glyphosate	MIP	✓	*	✓	✓

Table 1: List of sorbent types required for each target compound and sorbent availability for each sampling device or technique.

***CLAM disks may be available by custom order**

[CC, Chemcatcher®; CLAM, Continuous Low-Level Aquatic Monitoring; HLB, hydrophilic-lipophilic balance; SDB-RPS, styrene divinylbenzene- reverse phase sulfonate; SPEbot, solid phase extraction robot]

5a. Scientific Uncertainty

Results from this comparison study will inform the Board of Forestry about detections and concentrations of reforestation herbicides in managed post-fire environments to determine whether water quality objectives are maintained under current practice. Additionally, this study will inform practitioners about the pros and cons of using the various sample collection strategies to determine which is most appropriate for post-fire and general forestry uses.

The presumption that reforestation herbicide uses on large-scale Emergency Notices and substantially damaged THPs do not cause individual or cumulative impacts has not been tested. This monitoring project will begin to assess this presumption and provide important datasets with which to assess the efficacy of the FPRs at protecting the beneficial uses of water in post-fire environments.

This study focuses on collecting samples using various methods to best assess water quality objectives in the Central Valley Region which are derived from acute toxicity exposures (the concentration of each herbicides that causes mortality in 50% of the test organisms after 96-hours). Chronic toxicity exposure refers to exposure timescales of weeks to months, typically with lower concentrations, and may also be used as water quality objectives, however long-term data for such uses is rarely collected. Focusing on acute toxicity will target the highest concentrations that can be detected. However, the findings may also present data relevant to chronic toxicity which could possibly be a more relevant water quality objective under these conditions.

This monitoring project will address knowledge gaps associated with limited comparisons between herbicide concentrations derived from various sampling techniques (grab, continuous, or composite sampling) that are collected over a time-scale relevant to water quality objectives in post-fire environments.

Passive sampling is a well-established method for assessing presence/absence of aquatic pesticides and may be used for durations that may be more relevant to chronic toxicity exposures (weeks). However, the mass derived from a sampler does not have a corresponding volume of water sampled, therefore this method for computing a resulting concentration is not straightforward. If statistically significant correlations can be made between uptake of herbicide on a passive sampler to concentrations measured in the stream by other means, it would represent an important improvement on this technique for estimating concentrations.

5b. Geographic Scope

The geographic scope of this study will include three sampling locations visited multiple times. An effort will be made to distribute sampling locations throughout several geographic areas; however, the final locations will depend several factors including reforestation activities and planned herbicide application by private landowners. Sampling sites will be located with the intention of maximizing the likelihood of detecting in-stream concentrations for this study because it is necessary to have detectable concentrations with which to make comparisons. The specific sampling sites will be determined once the general planning watersheds where herbicides will be applied have been identified, and exact sampling locations will be determined additionally based on logistics, safety, and access considerations.

One potential distribution of sampling sites could include sites in the Feather River watershed in the western Sierra Nevada Range within the Dixie or North Complex Fire zones, the Thomes Creek watershed on the eastern California Coastal Mountain Range within the August Complex fire, or the Cosumnes River Watershed in the western Sierra Nevada Range within the Caldor Fire footprint. These general locations are subject to change based on planned and actual herbicide applications. Such a distribution could account for geographic distribution, while also mimicking the distribution of the most recent large-scale wildfires in California (fig. 3).

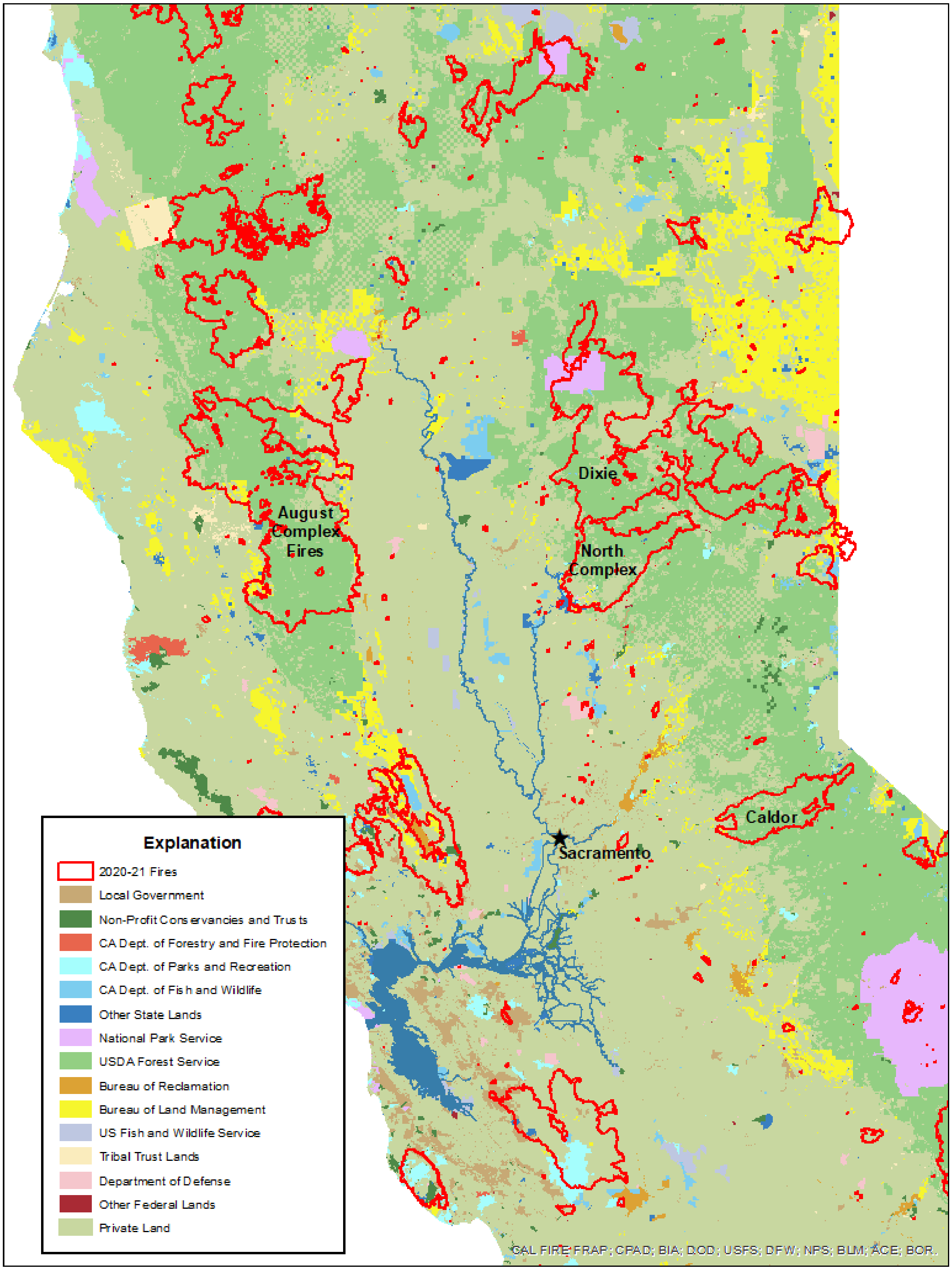

Figure 3. Locations of 2020–2021 wildfires in northern California and land ownership.

6. Collaborators and Project Feasibility

The collaborators involved in this proposal successfully completed a prior study that included deploying and analyzing over 80 Chemcatcher® disks for a suite of 155 pesticides or pesticide degradates in Sierra Nevada foothill streams between 2018 and 2019 (De Parsia et al., in review). The CVRWQCB purchased a supply of Chemcatcher® passive sampler devices during that study that will be adequate for the proposed study design. The CVRWQCB also already owns four CLAMs which will greatly reduce the equipment cost required for our proposed study. In the previous joint study, the USGS OCRL demonstrated the ability to analyze for pesticides with limits of detection between 0.002 and 0.004 micrograms per disk for Chemcatcher® samples and method detection levels between 0.0005 and.0105 micrograms per liter for surface water grab samples. For reference, the lowest EPA OPP aquatic life benchmark for one of the pesticides to studied in the proposed project is 0.29 micrograms per liter.

Staff from the CVRWQCB will be responsible for field sampling, coordination with landowners/managers, and monitoring pesticide-use notifications in study region watersheds to plan sampling events. Staff from the USGS will be responsible for preparation of sampling devices, field sampling, sample analysis, and report writing. The proposed study is designed with flexibility in mind to allow for a scalable project that can be adapted due to challenges with site accessibility, weather, or consumables availability. This, combined with the completion of past projects between collaborators demonstrates the feasibility of this study.

7. Project Deliverables

- Post event check-ins (3): Informal updates with a summary of devices tested, preliminary pesticide results, pictures, and event conditions to be submitted within three months of each sampling event.
- Publish all numerical water quality data generated from the proposed project to publicly available databases including the CEDEN and the U.S. Geological Survey's ScienceBase online data repository within one year of the final analysis results. Surface-water pesticide results will be uploaded to the USGS National Water Information System.
- Presentation to EMC after completion of sampling and analysis.
- Peer reviewed journal article or USGS report

8. Project Timeline

The timeline for the proposed project is provided below with times referencing calendar years. Because the project is reactive in nature with respect to precipitation, wildfires, and post-fire herbicide application, exact timing of the sampling could be advanced or delayed based on judgement of the principal investigators. If the sampling window is delayed due to contracting, the timeline below will be delayed by a length of time equal to the length of the delay. For example, if contracting does not begin until Q2 2022, then the final deliverable will be due Q1 2025 instead of Q4 2024 as shown below.

Task	Q1 22 (Jan-Mar)	Q2 22 (Apr-Jun)	Q3 22 (Jul-Sep)	Q4 22 (Oct-Dec)	Q1 23 (Jan-Mar)	Q2 23 (Apr-Jun)	Q3 23 (Jul-Sep)	Q4 23 (Oct-Dec)	Q1 24 (Jan-Mar)	Q2 24 (Apr-Jun)	Q3 24 (Jul-Sep)	Q4 24 (Oct-Dec)
Contracting												
Obtain consumables												
Final site selection												
Method optimization												
Sample collection			Base-flow*	First flush	Spring storm		Base-flow*					
Sample analysis												
Presentation of results												
Public Data Release												
Report writing												

* If contracting is not complete in time to allow for a summer/fall 2022 baseflow sample event then the baseflow sample event can be pushed to summer 2023.

9. Requested Funding

See tables below:

Personnel and Fringe benefits

Employee Name/Expense Category	Organization	Task Name	Fiscal Year	Hours	Hourly Rate	Hourly Total	Leave Dist/Fringe Benefits	Total	Total (Gross)
Chemist (GS14)	USGS	Sample Analysis	2022	100.0	$ 85.89	$ 8,588.68	$ 1,846.57	10435	$ 18,718.90
Hydrologist (GS12)	USGS	Sample collection	2022	80.0	$ 66.52	$ 5,321.81	$ 1,144.19	6466	$ 11,598.81
Hydrologist (GS11)	USGS	Sample collection & project mgmt.	2022	170.0	$ 41.62	$ 3,329.78	$ 715.90	4046	$ 7,257.21
Chemist (GS11)	USGS	Sample Analysis	2022	100.0	$ 43.88	$ 4,388.31	$ 943.49	5332	$ 9,564.27
Physical Scientist (GS7)	USGS	Sample Analysis	2022	100.0	$ 24.56	$ 2,455.50	$ 527.93	2983	$ 5,351.73
Chemist (GS12)	USGS	Sample Analysis	2022	100.0	$ 64.76	$ 6,475.99	$ 1,392.34	7868	$ 14,114.33
Hydrologic Technician (GS7)	USGS	Sample collection	2022	80.0	$ 30.11	$ 2,408.48	$ 517.82	2926	$ 5,249.25
Senior Environmental Scientist	WB	Sample collection	2022	80.0	$ 72.23	$ 5,778.40	$ 2,022.44	N/A	$ 7,800.84
Environmental Scientist	WB	Co-PI	2022	170.0	$ 37.11	$ 6,308.70	$ 2,208.05	N/A	$ 8,516.75
Engineering Geologist	WB	Project liaison	2022	80.0	$ 61.29	$ 4,903.20	$ 1,716.12	N/A	$ 6,619.32
Chemist (GS14)	USGS	Sample Analysis	2023	100.0	$ 88.46	$ 8,846.34	$ 1,901.96	10748	$ 19,280.47
Hydrologist (GS12)	USGS	Sample collection	2023	80.0	$ 68.52	$ 5,481.46	$ 1,178.51	6660	$ 11,946.78
Hydrologist (GS11)	USGS	Sample collection	2023	80.0	$ 42.87	$ 3,429.67	$ 737.38	4167	$ 7,474.93
Chemist (GS11)	USGS	Sample Analysis	2023	100.0	$ 45.20	$ 4,519.96	$ 971.79	5492	$ 9,851.19
Physical Scientist (GS7)	USGS	Sample Analysis	2023	100.0	$ 25.29	$ 2,529.17	$ 543.77	3073	$ 5,512.28
Chemist (GS12)	USGS	Sample Analysis	2023	100.0	$ 66.70	$ 6,670.27	$ 1,434.11	8104	$ 14,537.75
Hydrologic Technician (GS7)	USGS	Sample collection	2023	80.0	$ 31.01	$ 2,480.73	$ 533.36	3014	$ 5,406.73
Hydrologist (GS11)	USGS	Report writing	2023	166.3	$ 42.87	$ 7,129.43	$ 1,532.83	8662	$ 15,538.50
Senior Environmental Scientist	WB	Sample collection	2023	80.0	$ 76.03	$ 6,082.40	$ 2,128.84	N/A	$ 8,211.24
Environmental Scientist	WB	Co-PI	2023	170.0	$ 39.06	$ 6,640.20	$ 2,324.07	N/A	$ 8,964.27
Engineering Geologist	WB	Project liaison	2023	80.0	$ 64.52	$ 5,161.60	$ 1,806.56	N/A	$ 6,968.16
Total:									$208,483.69

Note: USGS will contribute up to $36,000 in matching funds, but matching fund contributions cannot be guaranteed.

Operating Expenses

Equipment	Organization to purchase	Fiscal Year	Quantity	Cost per unit	Total
Chemcatchers SPE disks, 20/pack	USGS	2022 and 2023	1	$ 325.73	$ 325.73
CLAM SPE cartridge	USGS	2022 and 2023	20	$ 79.00	$ 1,580.00
Lab Consumables	USGS	2022 and 2023	1	$ 4,000.00	$ 4,000.00
Additional CLAM	Waterboard	2022 and 2023	2	$ 8,532.00	$ 17,064.00
Total					$ 22,969.73

Operating Expenses (Already purchased)

Equipment (Already purchased)	Quantity	Cost	Total
CLAM	4	$ 8,532.00	$ 34,128.00
Chemcatchers	8	$ 787.00	$ 6,296.00
SPE Bot	3	$ 500.00	$ 1,500.00
Total			$ 41,924.00
Total Operating Costs			$ 41,924.00

Indirect Costs

Employee Name/Expense Category	Org.	Task Name	Fiscal Year	Hours	Hourly Rate	Hourly Total	Leave Dist./Fringe	Total	Total (Gross)
Associate Governmental Program Analyst	WB	Contract Management	2022	20	$ 41.20	$ 824.00	$ 288.40	N/A	$ 1,112.40
Associate Governmental Program Analyst	WB	Contract Management	2023	20	$ 43.40	$ 868.00	$ 303.80	NA	$ 1,171.80
Total									$ 2,284.20

In-kind contribution:	Water Board Matching Funds
2022 personnel	$ 22,936.91
2023 personnel	$ 24,143.67
2022 WB Travel	$ 500.00
2023 WB Travel	$ 500.00
Operating Expenses	$ 40,424.00
Indirect Costs	$ 2,284.20
Total Matching Funds	$ 90,788.78

Total Costs

Cost Type	Total
Personnel	$ 208,483.69
Operating Expenses	$ 64,893.73
Indirect Costs	$ 2,284.20
Travel	$ 2,000.00
Total	$ 277,661.62
Total funds requested	**$ 186,872.84**

Appendix

A1. Applicable Critical Question, Theme, FPR, or Policy

EMC Themes:

#1: WLPZ Riparian Function. "The FPRs have been developed to ensure that timber operations do not potentially cause significant adverse site-specific and cumulative adverse impacts to the beneficial uses of water…"
#2: Watercourse Channel Sediment. "A primary goal of these regulations has been to limit the delivery of management-related sediment to watercourse channels in California."
#5: Fish Habitat. "The critical questions included under this theme relate to maintaining and/or restoring the quality and connectivity of foraging, rearing, and spawning habitat…"

Critical Questions from EMC Strategic Plan (2018):

5 (b) Are the FPRs and associated regulations effective in maintaining and restoring the distribution of foraging, rearing and spawning habitat for anadromous salmonids?

Porter Cologne Water Quality Act § 13240

Each regional board shall formulate and adopt water quality control plans for all areas within the region. Such plans shall conform to the policies set forth in Chapter 1 (commencing with Section 13000) of this division and any state policy for water quality control. During the process of formulating such plans the regional boards shall consult with and consider the recommendations of affected state and local agencies. Such plans shall be periodically reviewed and may be revised.

895 (definitions):

*"**Water Quality Requirements** means a water quality objective (narrative or numeric), prohibition, TMDL implementation plan, policy, or other requirement contained in a water quality control plan adopted by the Regional Board and approved by the State Water Board."*

896 (a) Forest Practice Rules Purpose:

"The purpose of the Forest Practice Rules is to implement the provisions of the Z'berg-Nejedly Forest Practice Act of 1973 in a manner consistent with other laws, including but not limited to, the Timberland Productivity Act of 1982, the California Environmental Quality Act (CEQA) of 1970, the Porter Cologne Water Quality Act, and the California Endangered Species Act."

FPR 898.2 Special Conditions Requiring Disapproval of Plans, §(h):

"implementation of the plan as proposed would cause a violation of any requirement of an applicable water quality control plan adopted or approved by the State Water Resources Control Board."

State and Regional Water Quality Control Boards priorities listed in Appendix C of the EMC Strategic Plan (2018), pages 43-44:

"…it is necessary to evaluate the effectiveness of the FPRs and associated regulations in sustaining or improving aquatic ecosystem and watershed conditions, as measured through factors such as…restoring impaired aquatic and riparian function" "…Additional studies and methods are needed <u>to evaluate known or suspected water quality factors in timberland watersheds, such as…management practices applied during and after timber harvest activities in wildfire-affected areas.</u>"

Central Valley Water Quality Control Plan (Basin Plan) Section 4-112:

> *"… the Board will use the best available technical information to evaluate compliance with the narrative objectives. Where valid testing has developed 96-hour LC50 values for aquatic organisms (the concentration that kills one half of the test organisms in 96 hours), the Board will consider one tenth of this value for the most sensitive species tested as the upper limit (daily maximum) for the protection of aquatic life…"*

916.3, 936.3, 956.3 General Limitations Near Watercourses, Lakes, Marshes, Meadows and Other Wet Areas [All Districts]

> *"The quality and beneficial uses of water shall not be unreasonably degraded by Timber Operations. During Timber Operations, the Timber Operator shall not place, discharge, or dispose of or deposit in such a manner as to permit to pass into the water of this state, any substances or materials…in quantities deleterious to fish, wildlife, or the quality and beneficial uses of water. All provisions of this article shall be applied in a manner which complies with this standard."*

Technical Rule Addendum No. 2: Cumulative Impacts Assessment Guidelines

Section A (Watershed Effects):

> *"…In some cases, measurements may be required for evaluation of the potential for significant adverse Effects. The evaluation of Impacts to watershed resources is based on significant adverse on-site and off-site Cumulative Impacts on Beneficial Uses. Additionally, the Plan must comply with the quantitative or narrative water quality objectives set forth in an applicable Water Quality Control Plan.*

Additionally, subsection (d) (Chemical Contamination Effects) states:

> *"Potential sources of chemical CWEs include run-off from roads treated with oil or other dust-retarding materials, direct application or run-off from pesticide treatments, contamination by equipment fuels and oils, and the introduction of nutrients released during burning of Slash and Woody Debris or wildfire from two or more locations."*

A2. Sampling Device Details

Disk Preparation

Before deploying, polytetrafluoroethylene (PTFE) disk holders will be cleaned, and disks will be cleaned and conditioned prior to use. PTFE disk holders will be cleaned with warm water and detergent, rinsed with tap water, rinsed with methanol, then rinsed with organic-free water (OFW) before use. Disks for use in Chemcatcher® will be cleaned and conditioned using solvents recommended by the disk manufacturer. Cleaning of disks will be done using 47mm filter holders (Diskcover-47, Restek®, Bellefonte, Pennsylvania) on a vacuum manifold. Conditioning solvents will be allowed to soak into the disk for one minute before being drawn though the disk under gentle vacuum. Cleaned disks will then be inserted into the PTFE disk holders until use and sealed to keep the SPE media wet until deployment using a threaded PTFE cap.

Deployment Process

Chemcatchers® will be transported to sample sites on wet ice with transport lids affixed to the PTFE disk assemblies, wrapped in foil, then sealed in plastic bags. Chemcatcher® cages and disks are to be installed by two-person field teams. Upon arrival at a sample location, one team member (dirty hands) will put on clean gloves, rinses the stainless steel Chemcatcher® cage in native stream water, then secures the cage in an appropriate location. The other team member (clean hands) removes the still-sealed PTFE disk assembly from a cooler and will bring them to the stream bank. Using clean gloves, the clean hands team member removes the PTFE disk assemblies from their protective plastic bags and foil wrappers. The clean hands team member then removes the transport lid and hands the uncovered PTFE disk assembly to the dirty hands team member, who installs the disk assembly in the submerged stainless-steel cage, taking care to minimize the amount of time the disk was exposed to air.

For passive sampler field blanks, disks are to be transported to the field site in their PTFE disk assemblies, exposed to air by the clean hands team member for approximately 10 minutes while the environmental disk assembles are being deployed, then re-sealed, and transported back to the laboratory on wet ice. The process will then be repeated using the same field blank disk during the retrieval of the corresponding environmental passive sampler.

Passive samplers will be deployed in streams for approximately 4 days. Retrieval of the Chemcatchers® will be the reverse of the deployment process described above: the dirty hands team member retrieves the cage from the stream, removes the disk assembly from the stainless-steel cage, then hands the disk assembly to the clean hands team member. The clean hands team member quickly seals the disk assembly with a clean PTFE transport lid, then wraps the assembly in foil and places the disk assembly in a clean plastic bag labeled with the sample site, deployment date and time, retrieval date and time, and disk configuration. The sealed disk assemblies will then be transported to the analyzing laboratory on wet ice for processing and analysis by LC-MS/MS.

Post-Deployment Disk Processing

After deployment and recovery, the SPE disks will be stored in a freezer at -20 °C until they are ready to be processed. Each SPE disk will be freeze-dried to remove remaining water before elution, then eluted using a 47 mm filter holder on a vacuum manifold with a collection tube placed below the filter holder to catch the eluent. After inserting the freeze-dried disk into the filter holder, the disk will be spiked with 50 microliters (µL) of a 2 nanogram per microliter (ng/µL) surrogate solution containing $^{13}C_3$-atrazine, di-*N*-propyl-d_{14}-trifluralin, and $^{13}C_4$-fipronil and 50 µL of a 1 ng/µL solution containing d_4-imidacloprid. The disk will then be eluted with two 10 milliliter (mL) aliquots of a 1:1 (volume/volume) mixture of methanol and acetonitrile. The extract is then concentrated to near-dryness and reconstituted with an addition of 200 µL of acetonitrile. 20 µL of a 10 ng/µL solution containing d_{10}-acenaphthene and d_{10}-phenanthrene, and 20 µL of a 5 ng/µL solution containing d_3-chlothianidin will be added as internal standards prior to transferring the extract to an autosampler vial for analysis. Sample extracts are to be stored in a freezer at -20 °C until analysis (up to 30 days).

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