California Environmental Laboratory Accreditation Program (ELAP)

Environmental Laboratory Technical Advisory Committee (ELTAC) Meeting

April 17, 2019

NOTICE OF ENVIRONMENTAL LABORATORY TECHNICAL ADVISORY COMMITTEE (ELTAC) MEETING

April 17, 2019
10:00 a.m. – 5:00 p.m.
(or until completion of business)

Location 1	**Location 2**
California Environmental Protection Agency Building	Metropolitan Water District of Southern California
Room 2540	700 North Alameda Street, Room US-2456
Sacramento, CA 95814	Los Angeles, CA 90012

The Environmental Laboratory Accreditation Program (ELAP) will host a meeting of its technical advisory committee, as noted above. The notice and agenda for this meeting and others can be found at www.waterboards.ca.gov/elap. For further information regarding this agenda, see below or contact ELAP at elapca@waterboards.ca.gov or (916) 323-3431.

This meeting is available via webcast at https://video.calepa.ca.gov/.

AGENDA

ITEM 1 – Call to Order/Roll Call
ITEM 2 – Public Comments on Items Not on Agenda
ITEM 3 – Approval of November 13, 2018 and December 13, 2018 Meeting Minutes
ITEM 4 – DELAPO Report (updates on administrative activities, draft regulations, enforcement, new method offerings, USEPA 2017 Method Update Rule)
ITEM 5 – ELTAC Workgroup Updates
ITEM 6 – ELTAC Subcommittee on QMS Update
ITEM 7 – State Water Resources Control Board, Division of Water Quality: 2018 Draft Toxicity Provisions
ITEM 8 – State Water Resources Control Board, Division of Water Quality: PFAS Phased Investigation Approach
ITEM 9 – State Water Resources Control Board, Division of Drinking

Water: PFAS Phased Investigation Approach
ITEM 10 – Central Valley Regional Water Quality Control Board: Non-Point Source Aquatic Screening and Monitoring
ITEM 11 – Central Valley Regional Water Quality Control Board: USEPA Sufficiently Sensitive Methods Rule
ITEM 12 – State Water Resources Control Board, Division of Drinking Water: Legislative mandate of microplastics, child day care facilities and Detection Limit Reporting survey
ITEM 13 – Close – Review Action Items

Action may be taken on any item on the agenda. The time and order of agenda items are subject to change at the discretion of the ELTAC Chair and may be taken out of order. The meeting will be adjourned upon completion of the agenda, which may be at a time earlier or later than posted in this notice.

In accordance with the Bagley-Keene Open Meeting Act, all meetings of ELTAC are open to the public.

Government Code section 11125.7 provides the opportunity for the public to address each agenda item during discussion or consideration by ELTAC prior to ELTAC taking any action on said item. Members of the public will be provided appropriate opportunities to comment on any issue before ELTAC, but the ELTAC Chair may, at his or her discretion, apportion available time among those who wish to speak. Individuals may appear before ELTAC to discuss items not on the agenda; however, ELTAC can neither discuss nor take official action on these items at the time of the same meeting [Government Code sections 11125 and 11125.7(a)].

The meeting locations are accessible to the physically disabled. A person who needs a disability-related accommodation or modification in order to participate in the meeting may make a request by calling the ELAP general phone line at (916) 323-3431 or emailing elapca@waterboards.ca.gov. Providing your request at least five business days before the meeting will help to ensure availability of the requested accommodation.

Webcast Information

Webcast	**https://video.calepa.ca.gov/**

ENVIRONMENTAL LABORATORY ACCREDITATION PROGRAM
ELTAC MEETING
Wednesday, April 17, 2019 – 10:00 a.m.
CalEPA Building
1001 I Street, 2540
Sacramento, CA 95814
And
Metropolitan Water District of Southern California
700 North Alameda Street, Room US-2456
Los Angeles, CA 90012

Meeting Agenda

TIME	AGENDA ITEM	PRESENTER(S)
10:00am	**Call to Order/Roll Call** *Objective: Roll call.*	Stephen Clark, *Chairperson*
10:05am	**Public Comments on Items Not on Agenda**	Open
10:15am	**Approval of November 13, 2018 and December 13, 2018 Meeting Minutes** *Objective: Amend or approve minutes.*	Stephen Clark, *Chairperson*
10:20am	**Designated Laboratory Accreditation Program Officer Report** *Objective: Update members on recent ELAP developments and activities.*	Christine Sotelo, *DELAPO* Jacob Oaxaca, *ELAP*
10:40am	**ELTAC Workgroup Update** *Objective: Update members on Central Valley Water Board Pyrethroid Workgroup.*	Andrew Hamilton, *ELAP*
10:50am	**ELTAC Subcommittee Update** *Objective: Update members on Subcommittee on Alternative Quality Management System.*	Ronald Coss, *ELTAC Member*
12pm-1:15pm	Lunch	

TIME	AGENDA ITEM	PRESENTER(S)
1:15pm	**ELTAC Subcommittee Update (continued)** *Objective: Update members on Subcommittee on Alternative Quality Management System.*	Ronald Coss, *ELTAC Member*
1:45pm	**Regulatory Agency: State Water Board Division of Water Quality** *Objective: Advice regarding 2018 Draft Toxicity Provision.*	Karen Mogus, *Deputy Director*
2:15pm	**Regulatory Agency: State Water Board Division of Water Quality** *Objective: Information on PFAS Phased Investigation Approach*	Annalisa Kihara, *Section Chief*
2:30pm	**Regulatory Agency: Division of Drinking Water** *Objective: Information on New Regulatory Method Phasing*	Betsy Lichti, *Quality Assurance Section Chief*
2:45pm-3:00pm	Break	
3:00pm	**Regulatory Agency: Central Valley Regional Water Quality Control Board** *Objective: Information regarding Non-Point Source Aquatic Screening and Monitoring*	Daniel Whitley, *Environmental Scientist*
3:15pm	**Regulatory Agency: Central Valley Regional Water Quality Control Board** *Objective: Information regarding approach to USEPA Sufficiently Sensitive Method Rule.*	Dania Jimmerson, *Water Resource Control Engineer*
3:40pm	**Regulatory Agency: State Water Board Division of Drinking Water** *Objective: Information regarding legislative mandate of microplastics and lead in child day care facilities and Detection Limit Reporting survey.*	Melissa Hall, *Regulations Development Unit Chief*

TIME	AGENDA ITEM	PRESENTER(S)
4:00pm	**Close – Review Action Items** *Objective: Review any assignments generated during the meeting and adjourn.*	Stephen Clark, *Chairperson*

ELTAC Meeting

April 17, 2019

Sacramento and Los Angeles

ROLL CALL

Agenda Item #1

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MEETING PACKET

Roll Call

Name	Affiliation	Member Type	Present
Diane Anderson	APPL, Inc.	Rep	
Mindy Boele	CWEA	Rep	
Jill Brodt	Brelje and Race Laboratories	Rep	
Sean McCarthy	Division of Drinking Water	SRAE	
Gail Cho	CA Dept. of Fish and Wildlife	SRAE	
Stephen Clark	Pacific EcoRisk	Rep	
Ronald Coss	CWEA	Rep	
Huy Do	CASA	Rep	
Andy Eaton	Eurofins Eaton Analytical	Rep	
Miriam Ghabour	Metropolitan Water District of Southern California	Rep	
Bruce Godfrey	ACIL	Rep	
Anthony Gonzales	CAPHLD	Rep	
Rich Gossett	Physis Environmental	Rep	
David Kimbrough	Pasadena Water and Power	Rep	
Mark Koekemoer	Central Marin Sanitation District	Rep	
Bruce LaBelle	Dept. of Toxic Substances Control	SRAE	
Allison Mackenzie	Babcock Laboratories	Rep	
Christine Sotelo	CA ELAP	DELAPO	
Renee Spears	State Water Resources Control Board	SRAE	

Abbreviation	Member Type
DELAPO	Designated ELAP Officer, nonvoting
Scribe	Minutes (non-member)
SRAE	State Regulatory Agency Employee, nonvoting
Rep	Representative Member, voting

PUBLIC COMMENTS ON ITEMS NOT ON AGENDA

Agenda Item #2

Public Comments on Items Not on Agenda

Members of the public may address the Environmental Laboratory Technical Advisory Committee (ELTAC) regarding items that are not contained in the meeting agenda at this time.

However, ELTAC may not discuss or take action on any item raised during this public comment session, except to decide whether to place the matter on the agenda of a future meeting [Government Code sections 11125 and 11125.7(a)].

APPROVAL OF NOVEMBER 18, 2018 AND DECEMBER 18, 2018 MEETING MINUTES

Stephen Clark, Chairperson

Agenda Item #3

DELAPO REPORT

Christine Sotelo, ELAP

Agenda Item #4

Accomplishments since your last meeting

- Members submitted comments on 3rd preliminary draft regulations & attended draft regulations workshops
  - Thank you for your participation
  - More about draft regulations in the DELAPO report
- ELTAC Pyrethroid Workgroup & Subcommittee on Alternative QMS
  - More on this later
- The framework you established for State Regulatory Agency needs is working
  - More during DELAPO report & afternoon agenda items

What I'll cover today

- ***Updates***
  - Accreditation Process
  - Training Contract
  - Draft Regulations
  - Enforcement Guidance

- Purpose of California ELAP Accreditation
  - How ELAP updates offerings

- New ELAP Accreditation Offerings
  - PFAS analytical test methods
  - Method Update Rule

Accreditation Process Reminders

- Application
  - 90-day deadline
  - Certificates expiring in June: 20+ labs failed to comply with deadline
- ELAPCA@waterboards.ca.gov
  - ELAP's central line of communication, tracked daily
  - Triage emails to appropriate staff for response
- Amendment application
  - Add or remove to current scope (CCR § 64803)
  - Required fee

NV5/Dade Moeller Training Contract

- Outstanding partnership with ELAP
  - Multi-year training/assessment
  - Primary purpose train ELAP staff
  - Secondary purpose to help assess drinking water laboratories

- Start activity next fiscal year, July 1st

Draft Regulations Update

- 3rd Preliminary Draft Regulations Workshops held January 2019
- ELAP extended comment period at laboratory community request
  - Added extra time for comments
- Took the public comments to heart
  - 528 unique comments
- Thank you for your comments!

Enforcement Guidance

- We receive many referrals from State Regulatory Agencies
  - Agencies are actively reviewing data for validity, defensibility, historical recreation
- Notice of Violations
  - ELAP is issuing NOVs for failure to electronically upload data to Division of Drinking Water
- Citations are next step in enforcement actions

Awareness of Enforcement Areas

- Fraud/falsification of data
- Reporting results for non-accredited methods
- Repeat findings/not completing corrective action
- Not adhering to/maintaining Quality Assurance Manual
- Method deviations
  - Deviating from procedures
  - MDL's
  - IDOC
- Not adhering to QC criteria
- Improper use/maintenance of instrumentation and support equipment
- Traceability of analysis

What I'll cover today

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- ***Purpose of California ELAP Accreditation***
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Accreditation is for Regulatory Purpose

- Regulatory purpose means a statutory or regulatory requirement of a state board, office, or department, or of a division or program

- State Regulatory Agencies approve
  - Analytical test method for regulatory purpose
  - ELAP's accreditation offerings

- How does this work? Let's walk through the process…

Analytical Test Methods are Decided During the State Agency Regulatory Process

- The public, regulated entities, and the laboratories that perform the testing have the opportunity to comment during the development of permits, policies, and orders before adoption

- State Regulatory Agency/ELAP may convene to discuss analytical needs

- Some requirements are set in statute or regulations
  - Drinking and waste water methods set out in federal regulations
  - Other times, methods are set out in individual permits or orders or a detection limit is identified for which the method must meet

- It's ***not ELAP's responsibility, core function*** to inform laboratories (municipal or contracted) of new monitoring or state regulatory requirements

And During the Project Discussions (Client/Commercial Lab or Municipal Permittee Representative/In-House Lab)

- Questions to Ask
  - Why must I do the testing? What decision do I need to make? What are my method selection considerations?
- Method Selection Considerations
  - Regulatory Programs, Detection Levels, Project Objectives, Levels of Certainty, Previous Analytical Activities, Subsequent Analytical Activities
- Laboratory Capabilities and Method Selection
  - Laboratory Certifications or Accreditations, Sensitivity - Method Detection Levels, Selectivity (identification), Precision and Accuracy, Reproducibility, Reporting Capabilities
- Method not on ELAP's Accreditation Offerings?
  - Ask State Regulatory Agency/Client to request update to accreditation offering

ELTAC Plays a Critical Role

- *Proposed Framework for State Agency Requests to ELAP for New Analytical Methods and Lowered Reporting Limits*

- ELAP developed an SOP for the Framework
  - State Regulatory Agency submits request in writing to ELAP Chief

- State Agency is encouraged to coordinate with ELTAC Chairperson & DELAPO to propose an agenda item
  - State Agency can seek advice during ELTAC meeting
  - Longer, detailed discussions are directed to ELTAC workgroup

- There are several ELTAC items on today's agenda

ELAP Will Announce New Method Offerings

- ELAP will post updated Field of Testing form(s)
  - Always download latest version from ELAP webpage
- ELAP will post formal announcements
  - Posted to ELAP's webpage
  - Email subscription members

What I'll cover today

- Updates
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  - Enforcement

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- ***New ELAP Accreditation Offerings***
  - PFAS analytical test methods
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Per- and Polyfluorinated Alkyl Substances

- Announcement released on April 2, 2019
  - Drinking Water and Non-Drinking Water analysis
- New Field of Testing Forms 105, 111, & 117 uploaded to webpage

2017 USEPA Method Update Rule

- By May 31, 2019, ELAP will update offerings
- Pending meetings with State and Regional Water Quality Control Boards
- Relevant to the ELTAC Agenda Item #11 on USEPA Sufficiently Sensitive Method Rule

ELTAC WORKGROUP UPDATES

Agenda Item #5

CENTRAL VALLEY WATERBOARD PYRETHROID WORKGROUP

Andrew Hamilton, ELAP

Agenda Item #5

March 13, 2019

Dear ELAP-Accredited Laboratories,

The California Regional Water Quality Control Board - Central Valley Region (Central Valley Water Board) has adopted a Pyrethroid TMDL and Basin Plan Amendment that sets concentration goals for six pyrethroids in wastewater effluent and surface water. The Basin Plan Amendment (BPA) applies to municipal and agricultural discharges throughout the Central Valley. The BPA, which took effect on February 19, 2019, requires dischargers to begin monitoring for pyrethroids 2020 or sooner. The BPA sets low concentration goals for pyrethroids in discharge and receiving water, and therefore lower analytical reporting limits than commonly commercially available will be required for compliance monitoring. The minimum reporting levels (MRLs)[1] derived from the BPA are specified in Table 1. The Central Valley Water Board is requesting that laboratories submit performance-based method validation packages for analytical methods that can achieve these MRLs for pyrethroids in whole water (unfiltered) samples from surface waters and wastewater effluent. If chronic-based MRLs cannot be achieved, then acute-based MRLs will be accepted on an individual analyte basis. The Central Valley Water Board will consider methods for single laboratory use, but ultimately seeks a method that can be used statewide.

Laboratories interested in participating in compliance monitoring for the BPA must be accredited by the Environmental Laboratory Accreditation Program (ELAP). The Central Valley Water Board will review each validation package, and upon approval, the submitting laboratory will be eligible for accreditation under ELAP. Approved laboratories should then submit an amendment application for ELAP accreditation of the method. The Central Valley Water Board and ELAP will work closely to reduce the duration of the approval and accreditation process.

40 CFR 136 lists the following EPA-approved analysis methods for determining Clean Water Act compliance for permethrin: 608.2, 508, 525.1, 525.2, 1656, 1660, 608.3, and 625.1. Validation packages for an alternative test procedure or new method for total permethrin analysis will require US EPA approval. The other pyrethroids included in the BPA are not listed in 40 CFR 136, and therefore, the Central Valley Water Board has the authority to approve and will consider all validated methods for these analytes.

Validation packages should be prepared in accordance with EPA guidance for review and validation of alternative or new methods (USEPA, 2018a&b). The Central Valley Water Board requests that applicants complete and return the attached questionnaire to indicate their intent to participate in the method validation.

[1] MRLs represent the lowest concentration of a compound that can be quantitatively measured within prescribed quality control limits (USEPA, 2010).

Participating laboratories should submit their questionnaire to the Central Valley for review by April 15, 2019. Applicants should submit completed application packages to the Central Valley Water Board by September 30, 2019. Both the questionnaire and application package should be submitted to jessica.mullane@waterboards.ca.gov Validation packages will be reviewed on an ongoing basis, but priority will be given to those received by these deadlines.

Additional information may be provided to laboratories as the process continues. If you have any questions or would like to discuss, please contact Jessica Mullane at (916) 464-4691 or jessica.mullane@waterboards.ca.gov or Danny McClure at (916) 464-4751 or daniel.mcclure@waterboards.ca.gov.

Sincerely,

Original signed by
Daniel J. McClure, P.E.
Senior Water Resource Control Engineer
Central Valley Regional Water Quality Control Board

cc: Andrew Hamilton, ELAP, Division of Drinking Water, SWRCB
Melissa Morris, Office of Information Management and Analysis, SWRCB

Validation Package Requirements

Validation packages for both new and alternative methods must include the standardized quality control tests found in Appendix G of the EPA protocols. More detailed guidance on these tests when developing new methods can be found in Appendix G of USEPA, 2018b. Modified or alternative methods are required to meet or improve upon the quality control criteria specified in the original method.

Validation packages must include matrix effect samples to demonstrate that performance criteria can be met in the appropriate environmental matrix (wastewater and/or surface water) as well as reagent water or reference matrix. The measurement quality objectives that the Central Valley Water Board requires are summarized in Table 2.

1. Calibration linearity
The Central Valley Water Board requires a minimum of five calibration points and an $r \geq 0.995$ to demonstrate linearity. The five standards should span the expected sample range for each analyte, with the lowest calibration point below the MRL. Laboratories must include all calculations in the validation packages.

2. Calibration verification
The Central Valley Water Board requires 80-120% recovery of analytes in a mid-level calibration verification standard. Laboratories must include all calculations in the validation packages.

3. Absolute and relative retention time windows (for chromatographic analyses)
The Central Valley Water Board has no parameters for this component. Laboratories must include these values and the associated calculations for each analyte.

4. Initial precision and recovery (IPR)
Alternative Method
Laboratories must demonstrate their ability to meet or exceed the IPR precision and recovery criteria given for the EPA-approved reference method using both the alternative method and the corresponding approved method. If the reference method has no acceptance criteria, laboratories must demonstrate a recovery of 50-150% and a relative standard deviation (RSD) of less than 35%. Laboratories must perform the IPR test by analyzing four replicates of reagent water spiked with the analytes of interest. This IPR test should be performed for both the alternative method and the corresponding approved method.

New Method
The Central Valley Water Board requires a recovery of 50-150% and a relative standard deviation (RSD) of less than 35%. Laboratories must perform the IPR test in both a reference matrix (reagent water) and the sample matrix of interest. Laboratories must perform the IPR test by analyzing four replicates of reagent water spiked with the analytes of interest. Laboratories must use a concentration between one and five times the minimum level (ML) of quantitation of the new method and state this concentration in the method. Laboratories should analyze four spiked replicates of the matrix type to which the new method will be applied. The replicate samples should be spiked with the analytes of interest at a concentration one to five times the background concentration of the analytes in the sample or at one to five times the ML, whichever is greater.

5. Ongoing precision and recovery (OPR) (laboratory control sample)

Alternative Method

Laboratories must demonstrate that the alternative method can meet the OPR recovery criteria given in the EPA-approved reference method or 50-150% recovery and an RSD of less than 35%, whichever is more sensitive.

New Method

The Central Valley Water Board requires demonstration of ongoing precision and recovery in the form of a laboratory control sample (LCS). The recovery for this sample must be between 50-150% with an RSD of less than 35%. Laboratories must spike the LCS with the same concentration as that of the IPR samples.

6. Analysis of blanks

The Central Valley Water Board requires laboratories to demonstrate that the analyte concentrations in blank samples are below the requested MRL (Table 1).

7. Surrogate or labeled compound recovery

The Central Valley Water Board requires a surrogate recovery of 50-150% or better. Laboratories may submit historical control limits if available. Laboratories must identify the surrogates used and ensure its relevance to the analytes of interest.

8. Matrix spike and matrix spike duplicate precision and recovery (for non-isotope dilution analyses)

Alternative Method

Laboratories must demonstrate that the alternative method can meet the MS/MSD recovery and precision criteria associated with the EPA-approved reference method or the Central Valley Water Board criteria (Table 2), whichever is more sensitive. Laboratories must perform MS/MSD analysis for each matrix type. If acceptance criteria are not stated in the method, laboratories must demonstrate a recovery of 50-150% and a relative percent difference (RPD) of less than 35%.

New Method

The Central Valley Water Board requires a MS/MSD recovery of 50-150% and a relative percent difference (RPD) of less than 35%. Laboratories should spike the MS and MSD at a level that results in the concentration of the target analytes being at the MRL, one to five times the background concentration of a matrix sample, or at the level specified in the method, whichever is greater.

9. Method detection limit demonstration

Laboratories must perform a method detection limit (MDL) study for alternative and new methods. For both alternative and new methods, the MDL must be lower than the acute-based MRLs listed in Table 1.

Alternative methods must achieve an MDL that is less than or equal to the minimum level (ML) of the EPA-approved reference method, or less than 1/10 the regulatory compliance limit, whichever is greater. Laboratories must perform the MDL study in accordance with the with most recent MDL study requirements published in Appendix B of 40 CFR Part 136. As of August 2017, 40 CFR Part 136 Appendix B requires laboratories to analyze of a minimum of seven spiked samples and seven blanks to determine an MDL.

10. Minimum reporting limit verification
A minimum reporting limit (MRL) test must be performed either concurrently with MDL test or in a separate study. Laboratories must be able to demonstrate 50-150% recovery for samples spiked at the MRL for individual analytes (Table 1).

11. Standard operating procedure
Laboratories must include their standard operating procedure written in the EPA method.

Table 1. Requested minimum reporting levels (MRLs) calculated from BPA concentration goals[1]

Chemical[2]	**Requested MRL[3,4], Acute-Based (ng/L)**	**Requested MRL Chronic-Based, (ng/L)**
Bifenthrin	**1.3**	**0.2**
Cyfluthrin	**1.3**	**0.3**
Cypermethrin	**1.7**	**0.5**
Esfenvalerate	**3.3**	**0.5**
Lambda-cyhalothrin	**1.2**	**0.5**
Permethrin (total)	**10**	**1.7**

[1] See supplemental information for background information about the derivation of the MRL values from the Basin Plan Amendment concentration goals.
[2] Concentrations are total analyte concentrations, including all isomers.
[3] MRL is based on a Measurement Quality Objective (MQO) of 50%-150% recovery of spiked concentrations. Therefore, at or above the MRL, laboratories should obtain 50%-150% recovery or better (USEPA, 2010).
[4] Numbers reported to two significant figures.

Table 2. Quality Control Pyrethroids in Whole Water[1]

Laboratory Quality Control	Frequency of Analysis	Measurement Quality Objective
Tuning[2]	Per laboratory SOP	Per laboratory SOP
Calibration	Daily, or just prior to analysis; five or more standards spanning the sample result range[3], with the lowest standard at or below the MRL	r ≥0.995 (or r^2 ≥0.995, all curve types not forced through origin)
Calibration Verification	Per 10 analytical samples[4]	80-120%[5]
Laboratory Blank	Per 20 samples or per analytical batch, whichever is more frequent	<MRL for target analyte
Laboratory Control Sample[6]	Per 20 samples or per analytical batch, whichever is more frequent	50-150%
Matrix Spike	Per 20 samples or per analytical batch, whichever is more frequent	50-150%
Matrix Spike Duplicate	Per 20 samples or per analytical batch, whichever is more frequent	50-150%; RPD <35%
Surrogate[7]	Included in all samples and all QC samples	50-150% or better
Internal Standard	Included in all samples and all QC samples	Per laboratory procedure

[1]Modified from SWAMP's Quality Control and Sample Handling Tables: Synthetic Organic Compounds in Fresh and Marine Water (SWRCB, 2013).

[2]Mass spectrometry only

[3]Sample results above the highest standard are to be diluted and re-analyzed.

[4]Analytical samples include samples only and do not include clean-out or injection blanks.

[5]Limit applies to a mid-level standard; low-level calibration checks near the reporting limit may have a wider range that is project -specific

[6]Laboratory control samples must be matrix-specific.

[7]Laboratory historical limits for surrogate recovery may be submitted if available.

[8]A technical group consisting of regional, laboratory, and research representatives determined that field blanks do not provide technical value to a pyrethroids data set.

Supplemental Information

The concentration goals established in the BPA for bifenthrin, cyfluthrin, cypermethrin, esfenvalerate, lambda-cyhalothrin, and permethrin are freely dissolved concentrations, which are calculated from the whole water concentration following an equation described in the BPA Staff Report. As explained in Section 5.2.2 of the Staff Report, the freely dissolved pyrethroid concentration typically ranges from 1-30% of the whole water concentration, so the requested minimum reporting levels (MRLs) are adjusted upward to account for that.

The MRLs should be set at a level that captures the lower limit of the whole water concentration ranges. The requested method whole water concentrations were calculated and reported to two significant figures using the following equation, accounting for this proposed accuracy and assuming 30% freely dissolved concentration:

$$Whole\ Water\ Concentration = \left(\frac{BPA\ Concentration\ Goals}{30\%}\right) * 50\%$$

References

1. USEPA, 2018a. Protocol for Review and Validation of Alternate Test Procedures for Regulated Organic and Inorganic Analytes in Wastewater Under EPA's Alternate Test Procedure Program. U.S. Environmental Protection Agency. Office of Water, Engineering and Analysis Division. Washington, DC EPA 821-B-18-002. Available online from: https://www.epa.gov/sites/production/files/2018-03/documents/chemical-atp-protocol_feb-2018.pdf.

2. USEPA, 2018b. Protocol for Review and Validation of New Methods for Regulated Organic and Inorganic Analytes in Wastewater Under EPA's Alternate Test Procedure Program. U.S. Environmental Protection Agency. Office of Water, Engineering and Analysis Division. Washington, DC EPA 821-B-18-001. Available online from: https://www.epa.gov/sites/production/files/2018-03/documents/chemical-new-method-protocol_feb-2018.pdf.

3. USEPA, 2010. Technical Basis for the Lowest Concentration Minimum Reporting Level (LCMRL) Calculator. U.S. Environmental Protection Agency. Office of Water, EPA 815-R-11-001. Available online from: https://nepis.epa.gov/Exe/ZyPDF.cgi?Dockey=P100J7CA.txt.

4. SWRCB, 2013. Quality Control and Sample Handling Tables: Synthetic Organic Compounds in Fresh and Marine Water. California State Water Resources Control Board. Surface Water Ambient Monitoring Program (SWAMP). Sacramento, CA. Available online from: https://www.waterboards.ca.gov/water_issues/programs/swamp/docs/mqo/syn_org_com_water.pdf.

Central Valley Water Board Pyrethroid Method Development
Notice of Intent to Participate and Laboratory Background Survey

Laboratory Name and Address		
Laboratory Director		
Laboratory Point of Contact		
Point of Contact Phone		
Point of Contact Email		
Laboratory ELAP Accreditation Number		
Additional Accreditations (TNI, DoD, etc.)		
Does your lab currently process samples for Clean Water Act compliance?	☐ Yes	☐ No
Does your lab intend to process samples for Clean Water Act compliance?	☐ Yes	☐ No
Does your lab currently perform pyrethroid analysis?	☐ Yes	☐ No
How long has your lab been performing pyrethroid analysis?		
What matrix/matrices do you analyze?		
Please indicate which, if any, of the following pyrethroids you analyze.	☐ Bifenthrin	
	☐ Cyfluthrin, total	
	☐ Cypermethrin, total	
	☐ Esfenvalerate/Fenvalerate	
	☐ Cyhalothrin, lambda	
	☐ Permethrin, total	
Can you do all analytes within a single analysis?	☐ Yes	☐ No
Please indicate your extraction process(es).	☐ Separatory funnel What solvent?	
	☐ Solid Phase What solid phase?	
	☐ Continuous Liquid What solvent?	
Clean ups	☐ Yes	☐ No

Multiphasic extraction	☐ Yes, combine for total.	☐ No, dissolved only.
Please indicate which instrumentation you use in your analysis.	☐ GC-ECD	☐ HPLC
	☐ GC-MS	☐ LC-MS
	☐ GC-MSMS	☐ LC-MSMS
Calibration	Curve type?	
	Minimum number of points?	
	Low standard corresponds to reporting limit/PQL/ML?	
What are the control limits for your LCS?		
Are these control limits the same for your pyrethroid method?	☐ Yes	☐ No
Do you use a full-list spike?	☐ Yes	☐ No
What are the control limits for your surrogates?		
Are these control limits the same for your pyrethroid method?	☐ Yes	☐ No
What are your current reporting limits for the following analytes?	***Analyte***	***Reporting Limit***
	Bifenthrin	
	Cyfluthrin, total	
	Cypermethrin, total	
	Esfenvalerate/Fenvalerate	
	Cyhalothrin, lambda	
	Permethrin, total	
Please refer to Central Valley Water Board method request. If your current operations do not meet the requirements outlined in the request, how do you propose to address this in your application?		

Submit completed questionnaire to: Jessica.Mullane@waterboards.ca.gov

ELTAC SUBCOMMITTEE ON ALTERNATIVE QMS

Agenda Item #6

PROGRAM PERSPECTIVE

Christine Sotelo, ELAP

The NELAC Institute (TNI) Laboratory Standard Copyright

- TNI document is included by reference in ELAP's 3rd preliminary draft regulation

- Copies are available for viewing at
  - Regional Water Quality Control Board Offices
  - Division of Drinking Water District Offices
  - CalEPA Library in Sacramento

- TNI has offered California laboratories free 6-month membership
  - Discounted rate on the TNI Standard document

Ground Rules

1. ELAP does not support a dual track system
2. Critical Elements for Quality Management System
3. Consensus
4. Time is of the Essence

April 2019

The California Quality Management System:
Administrative Efficiency Meets Data Quality for the Protection of Public Health & the Environment

Presentation made to the Environmental Laboratory Technical Accreditation Committee (ELTAC)
April 17, 2019

By:
Ron Coss – CA QMS Chair
Amber Baylor – CA QMS Subcommittee Member
Bill Ray – CA QMS Subcommittee Member

Agenda

ELTAC Meeting Presentation Schedule

Wednesday, April 17	
Review of the December 13, 2018 Meeting	**5 min**
CA QMS Committee Formation	**5 min**
CA QMS Team, Timeline, & Critical Elements	**10 min**
CA QMS Article 5	**40 min**
Framework within TNI	10 min
CA QMS Article 5 Review	20 min
Additional Elements	10 min
Structured Discussion After Lunch	**30 min**

December 13, 2018 ELTAC Meeting

Motion Review

Motion by Ron Coss

ELTAC form a workgroup to create a tier of standards based on TNI and they be given a timeframe to report back to the full committee that will allow us to move forward to the Water Board. The committee will begin work in a timely manner and TNI based.

- Motion Seconded by Huy Do

Motion Amendment by Jill Brodt

There will be an emphasis of the Quality Management System workgroup be applicable to all ELAP labs. The focus be for all ELAP labs. So, don't do any work for a dual system.

- Motion passes through ELTAC 9-4-1

The CA QMS Subcommittee was the first ELTAC Subcommittee since the formation of ELTAC on March 23, 2016.

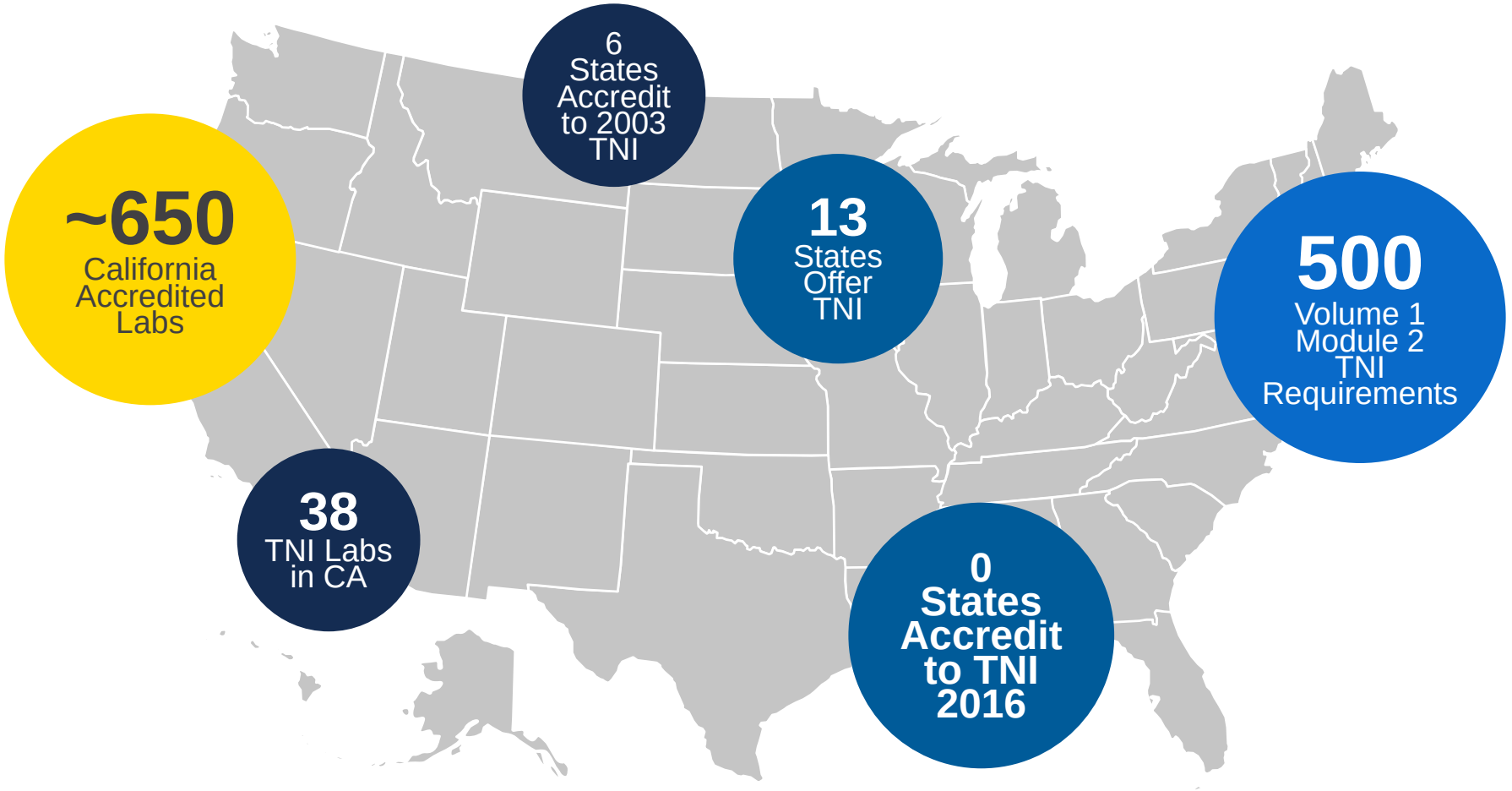
The official creation represents an open and transparent public process.


There are
39.5 Million People in California,
189,454 Miles of Streams,
& ~650 Accredited Laboratories.
“Start with Why”
-Simon Sinek

Why Create the CA QMS?

The CA QMS was designed for California Laboratories.

The CA QMS was designed to be the GOLD standard for laboratory accreditation focused on data quality produced from laboratories in an administratively efficient manner.



CA QMS Team, Timeline, & Critical Elements

CA QMS Subcommittee Members

216 years combined professional laboratory experience

Ron Coss

CA QMS Chair
33 Years Experience

Amber Baylor

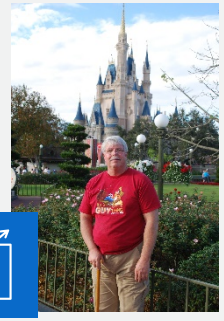
CA QMS Subcommittee Member
13 Years Experience

Mindy Boele

CA QMS Subcommittee Member
25 Years Experience

Josie Tellers

CA QMS Subcommittee Member
36 Years Experience



Bill Ray

CA QMS Subcommittee Member
46 Years Experience

Sushmitha Reddy

CA QMS Subcommittee Member
21 Years Experience

Huy Do

CA QMS Subcommittee Member
24 Years Experience

Paul Monroy

CA QMS Subcommittee Member
18 Years Experience

CA QMS Timeline

Subcommittee Creation
December 13, 2018 Vote to Create the Committee

2nd & 3rd Meetings
Reviewed 99 Recommendation by previous group & TNI Notes.

Final Meeting
Final Review of the CA QMS for incorporation into the 4th Draft ELAP Regulations

December 2018 | January 2019 | February 2019 | March 2019 | April 2019 | Today

First Meeting
Committee timeline, expectations, & work allocations.

4th and 5th Meetings
CA QMS Creation & Review.

Presentation on the CA QMS to ELTAC

CA QMS Articles

Article ONE

Definitions

Article TWO

Accreditation Process

Article THREE

Application Packages

Article FOUR

Accreditation Fees

Article FIVE

Quality System Standards

Article SIX

PT Study Requirements

Article SEVEN

Laboratory Personnel Requirements

Article EIGHT

Notification and Reporting

Article NINE

Trade Secrets

Article TEN

Sale or Transfer of Ownership of a Laboratory

15 Critical Elements of a QMS

Provided by Christine Sotelo at the December 13, 2018 ELTAC Meeting

Laboratory Operations

1. Materials and services assessed, found acceptable & traceable: Included TNI 2016 V1M2 4.2.8.4.a) and b) in CA QMS Article 5 §64808.00 b) 2)
2. Contract and subcontract requirements: CA QMS Article 5 §64808.00 j)

Management of Personnel

3. Laboratory objectives and structure: Included TNI 2016 V1M2 4.2.8.4.e) in CA QMS Article 5 §64808.00 b) 2)
4. Personnel roles, responsibilities and qualifications: Included TNI 2016 V1M2 4.2.8.4.g) in CA QMS Article 5§64808.00 b) 2)
5. Employee expectations: Included TNI 2016 V1M2 4.2.8.4.g) in CA QMS Article 5§64808.00 b) 2)
6. Complaint Resolution: Included TNI 2016 V1M2 4.2.8.4.h) & l) in CA QMS Article 5 §64808.00 b) 2)
7. Training and procedures preventing ethical misconduct: Included 2016 TNI V1M2 5.2.7 in CA QMS Article 5 §64808.00 b) 2)

Management of Data Quality

8. Find, correct and prevent problems: Included TNI 2016 V1M2 4.2.8.4.g) in CA QMS Article 5 §64808.00 b) 2)
9. Standard Operating Procedures: Included TNI 2016 V1M2 4.2.8.4.h) and V1M2 4.2.8.4.f)i thru xxiii in CA QMS Article 5 §64808.00 b) 2) & CA QMS §64808.00 e)
10. Quality policy: Included TNI 2016 V1M2 4,2,8,4.e) in CA QMS Article 5 §64808.00 b) 2)
11. Document Control: Included TNI 2016 V1M2 4.2.8.4.f) in CA QMS Article 5 §64808.00 b) 2)
12. Internal Audits: Included TNI 2016 V1M2 4.2.8.4.l) in CA QMS Article 5 §64808 b)3)
13. Non-conforming procedures: Included TNI 2016 V1M2 4.2.8.4.l) in CA QMS Article 5 §64808 b)3)
14. Data integrity investigations: Included TNI 2016 V1M2 4.2.8.4.h) and l) in CA QMS Article 5 §64808 b)3)

“Transparency is for those who carry out public duties and exercise public power. Privacy is for the rest of us.”

-Glenn Greenwald

The CA QMS Summary

Two Main Components form the Foundation of the System: Critical Quality Elements & Technical Methods

Key Partners

The CA QMS team are industry professionals who worked to create a standard based on TNI.

Participants and/or staff attended full TNI training & implementing requirements currently.

Key Activities

6 Meetings

Key Resources

Review of Previous Recommendations

Value Propositions:

- **Ethics Training Requirement**
- **Data Quality**
- **Administrative Efficiency**
- **Service Transparency**

Laboratory Business

Focus on Quality Systems

Based on Regulations

Local, State & Federal Regulations

Auditable

CA QMS retains the ability to be auditable by ELAP in an efficient and effective manner.

Includes transparency & consistency in ELAP Audits.

Quality System Components

Building on the 15 critical elements that ELAP provided, the CA QMS also includes requirement for sampling, quality assurance, and calibration requirements.

Technical Methods

Where the technical method is silent, the CA QMS through reference to TNI Volumes 3-7 fills in the gap.

CA QMS Article 5
The Heart of Data Quality

Article 5 Components

CA QMS Article 5 §64808.00: Quality System Standards

a) Laboratories seeking or holding accreditation shall comply with the quality management system as identified in b) through i)

b) Each laboratory shall have a quality manual formatted and with contents as follows

1) TNI, 2016, Rev. 2.1 Volume 1, Module 2, Section 4.2.8.3 a) through l), except e), and g);

2) TNI 2016, Rev. 2.1 Volume 1, Module 2, section 4.2.8.4 a) through r).

3) The laboratory must have a procedure in the quality manual and shall conduct internal audits in compliance with TNI 2016, Rev. 2.1 Volume 1, Module 2, section 4.14 . The audits may be scheduled as necessary however, shall be completed by the end of each 12-month portion of accreditation.

c) Laboratories are to adopt all quality assurance and quality control procedures; and criteria as specified in appropriate federal or state regulation; or in the federal or state regulatory approved methods the laboratory is accredited for.

d) Incorporate the contents of TNI, 2016, Rev. 2.1, Volume 1, Modules 3 through 7 (as appropriate for the test method) only where the test method or federal, state, and local regulation are silent on the requirement. In all cases requirements found in regulation or methods approved by regulation supersede requirements found in TNI, 2016, Rev. 2.1 Modules 3 through 7.

e) The laboratory shall have Standard Operating Procedures (SOP) for all the analytical methods the laboratory is seeking or holding accreditation. The format for all analytical SOPs shall contain discussion on the topics found in TNI, 2016, Rev. 2.1, Volume 1 Module 2, section 4.2.8.5.f).i) through xxiii. The SOP shall designate if any topic is not applicable to the method.

Article 5 Components

CA QMS Article 5 §64808.00: Quality System Standards

f) The laboratory is to employ the requirements in TNI, 2016, Rev. 2.1 Volume 1, Module 2 sections 5.5; 5.8; and 5.9. The quality management system shall include the requirements found in TNI, 2016, Rev. 2.1 Volume 1, Module 2, section 5.7 if any laboratory staff conduct sampling, even if on a temporary basis.
g) The laboratory shall incorporate data integrity training per TNI 2016, Rev. 2.1 Volume 1, Module 2, section 5.2.7. The training shall include ethics and ethical behavior training. The frequency shall be at least equal to the requirement in section 64812.00.(c).
h) Any section within the TNI, 2016, Rev. 2.1 standard that relates to the operation of a calibration laboratory are not applicable to this standard.
i) All items that are Notes in the TNI, 2016, Rev. 2.1 standard are not applicable or enforceable per the statement at the end of Volume 1, Module 2, section 1.2.

Article 5 Components

§64808.05 Onsite assessments of 64808.00

a) All on-site assessments will be conducted in accordance with the requirements found in General Requirements for Accreditation Bodies Accrediting Environmental Laboratories 2009 Rev. 0.1 V2M3 Section 6.

b) As allowed by Health and Safety Code section 100837, the laboratory may select a recognized third-party assessment organization. To be recognized, any third-party assessment organization shall possess any of the following

1) Training certificates for Basic Assessor as issued by TNI. The possession of a training certificate for TNI 2016, Rev. 2.1, Volume 1, Module 6 is required to assess under this module.
2) An approved assessor for a non-governmental accrediting body with evidence of training in ISO 17025:2005 or ISO 17025-2017.
3) An approved assessor for the federal Department of Defense or Department of Energy.
4) An approved assessor accepted by ELAP.

c) All assessments must be conducted within the 12th month to 20th month of accreditation.

Article 5 Components

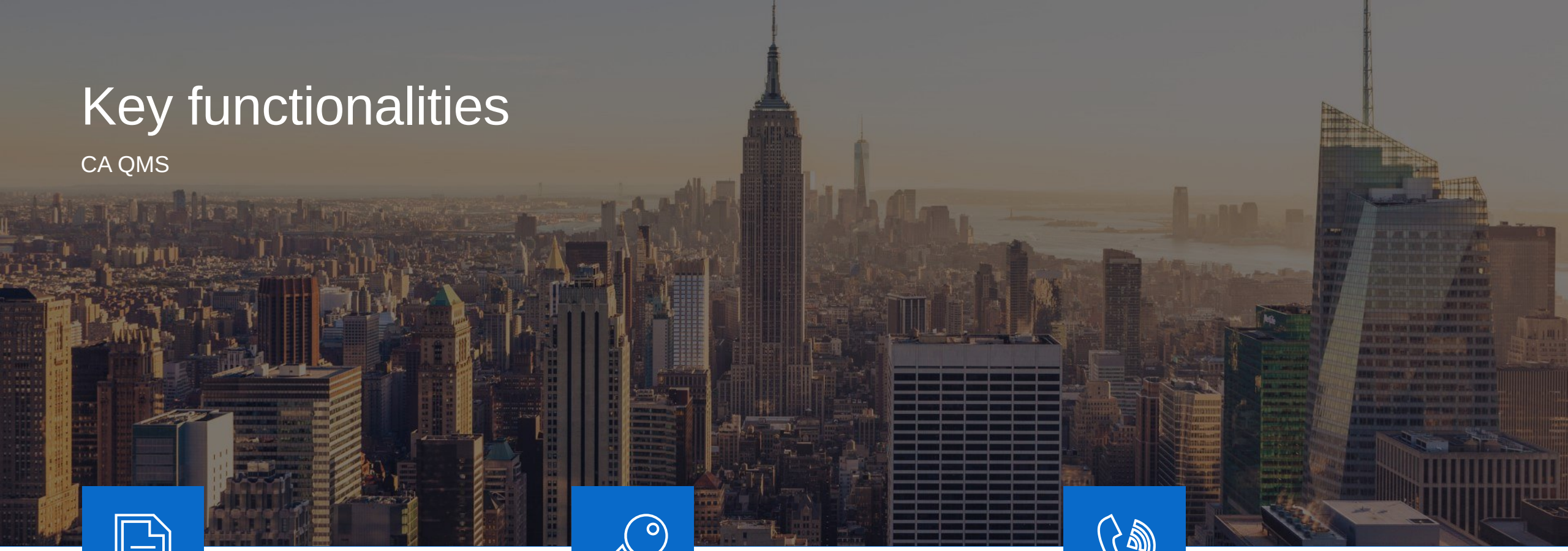
CA QMS Article 5 §64808.10 Service Transparency

§64808.10 Service Transparency

a) Within three (3) years of the adoption of these regulations, ELAP shall conform to the standards found in TNI 2016, Rev. 2.0 (a.k.a. TNI 2009, Rev. 0.1). ELAP may opt to conform to the standards found in ISO 17011:2017. If it does, then it shall also undergo assessment against the standard by a competent assessment organization.

Key functionalities

CA QMS



Data Quality

Most important feature

Technical Methods

Focus on the federally promulgated methods & regulatory requirements.

Service Transparency

ELAP Oversight.

The CA QMS **Means Business:** **Neat, Efficient & Focused on Data Quality**

Structured Discussion

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Article 1. Definitions
§64801. Definitions.

Article 2. Accreditation Process
§64802.00 Accreditation Process
§64802.05 Initial Accreditation
§64802.10 Renewing Accreditation
§64802.15 Amending Accreditation before Renewal
§64802.20 Acceptance of Another State or Federal Government Agency's Accreditation
§64802.25 Changes in laboratory name or location; structural alteration; or adding mobile or auxiliary facilities

Article 3. Application Packages
§64804 Application Packages

Article 4. Accreditation Fees
§64806. Accreditation Fees (fees are place-holders only)

Article 5. Quality System Standards
§64808 Quality System Standards
§64808.05 Onsite assessments of 64808.00
§64808.10 Service Transparency

Article 6. PT Study Requirements
§64810. PT Study Requirements.

Article 7. Laboratory Personnel Requirements
§64812.00 Personnel Training
§64812.05 Technical Manager Qualifications
§64812.10 Quality Manager Qualifications
§64812.15 Changes in Persons Identified as Technical Manager

Article 8. Notification and Reporting
§64814. Notification and Reporting.

Article 9. Trade Secrets
§64816. Trade Secrets.

Article 10. Sale or Transfer of Ownership of a Laboratory
§64818. Sale or Transfer of Ownership

Article 1. Definitions

§64801. Definitions.

a) Definitions found in *Management and Technical Requirements for Laboratories Performing Environmental Analyses*, The NELAC Institute (TNI), Rev 2.1, September 1, 2016, Volume 1, Modules 1 thru 7 apply to these standards. Any definition that does not exist in the standard are defined below. Any clarification to the definition in the above standard is cited below.

1) "Auxiliary facility" means any stationary or exempted mobile facility as defined under Mobile laboratory below, which meets the requirements in section 64802.25
2) "Batch" is defined as found in TNI 2016, Rev. 2.1, Volume 1, Module 2, section 3.
3) "Board" means the State Water Resources Control Board.
4) "California analyte" means a substance, organism, physical parameter, property, or chemical constituent required only by California statute or regulation.
5) "CA/NV AWWA" means the California/Nevada section of the American Water Works Association.
6) "CWEA" means the California Water Environment Association.
7) "DL" or "Limit of Detection" as found in the TNI standard means the Method Detection Limit (MDL). The laboratory is to follow the procedure as found in regulation or the regulatory approved method.
8) "ELAP" means the Environmental Laboratory Accreditation Program.
9) "Field(s) of Accreditation Matrix" is defined as the same as that listed for Quality System Matrix in Volume 1, Module 2, section 3.0 for the matrix portion of the complete Field of Accreditation definition (Matrix-Method/Technology-Analyte).
10) "International Standard" means the ISO standard 17025-2005.
11) "Laboratory Director" means the person who, for the laboratory is the person designated to perform the duties described in TNI 2016, Rev. 2.1, Volume 1 Module 2 for management and top management. Where staff is limited the position of Laboratory Director may be combined with the position of Quality Manager. If combined, then the person must perform all duties as required by TNI 2016, Rev. 2.1, Volume 1 Module 2 for each position.
12) "LOQ" or "Limit of Quantitation" as found in the TNI standard means the Minimum Level (ML); DLR; or Reporting Level (RL) specified by regulation.
13) "Mobile laboratory" means a non-stationary facility such as a vehicle; trailer; or other facility that can be transported. This does not include trailers or other facilities that are placed at the laboratory location and permanently connected to utility services.
14) "Owner" means for a commercial laboratory, any person who is a sole proprietor of a laboratory, or any person who holds a partnership interest in a laboratory, or any person who is an officer, or 5% (five percent) or more shareholder in a corporation which owns a laboratory. For governmental or publicly-owned laboratories the owner is the agency in which the laboratory resides organizationally.
15) "Owner's Agent" or "Agents of Owners" means those persons who have been designated by the Owner(s) of the laboratory to act in its behalf for purposes of complying with these

regulations or the statutes under which these regulations are adopted.

16) “Quality Manager” means the person who will perform the duties found in Volume 1, Module 2, section 4.1.7.1.
17) "Trade Secret" means any information that meets the definition in Section 6254.7(d) of the Government Code.
18) "Trailer" is the same as the definition given in Section 630, Vehicle Code.
19) “Unit(s) of Accreditation” means the same as Field of Accreditation as found in TNI 2016, Rev. 2.1, Volume 1, Module 2, section 3.
20) "Vehicle" is the same as the definition as given in Section 670, Vehicle Code.

b) All references to days, weeks, months or years are calendar based.

Article 2. Accreditation Process

§64802.00 Accreditation Process.

a) All laboratories seeking Initial or Renewal accreditation shall state at the time of application whether they wish accreditation under California ELAP accreditation; or via recognition allowed in section 64802.20 below.
b) All citations to the TNI standard incorporated by reference are from the *Management and Technical Requirements for Laboratories Performing Environmental Analyses*, The NELAC Institute (TNI), Rev 2.1, September 1, 2016
c) All on-site assessments will be conducted in accordance with the requirements found in General Requirements for Accreditation Bodies Accrediting Environmental Laboratories 2009 Rev. 0.1 V2M3 Section 6.
d) Regardless of which accreditation program chosen, all laboratories shall comply with the following based on the type of accreditation desired.

§64802.05 Initial Accreditation

a) A laboratory shall:
    1) Submit a complete application package in accordance with 64804;
    2) Submit performance test sample results in compliance with 64810;
    3) Submit a Quality manual in compliance with 64808; and
    4) Submit fee payment in accordance with 64806
b) The laboratory shall be assessed compliance with 64808 through an on-site assessment.
c) A laboratory may be granted interim accreditation prior to the on-site assessment in accordance with H&SC 100850(d) if any of the following information is provided with the application.
    1) Successful results from performance test samples
    2) Method performance data as required by TNI 2016, Rev. 2.1, Volume 1 Module 2, section 5.4.5.
    3) Initial Demonstrations of Capability as required by TNI 2016, Rev. 2.1, Volume 1, Module 3 through 7, section 1.6.1 as appropriate for the method(s). .

§64802.10 Renewing Accreditation

a) A laboratory shall:
    1) Submit a complete application package in accordance with 64804;
    2) Submit a Quality manual in compliance with 64808;
    3) Submit fee payment in accordance with 64806; and
    4) The laboratory shall be assessed compliance with 64810 performance test sample results.
    5) The report of actions taken as a result of an onsite assessment conducted during the second year of accreditation.

b) The requirements in a) above are to be submitted by the laboratory at least 90 days prior to the expiration date of the certificate.

§64802.15 Amending Accreditation before Renewal

a) If amending accreditation by the addition of one or more Fields of Accreditation a laboratory shall:
   1) Submit a notice of intent to amend by addition listing the requested Field(s) of Accreditation and any information that has changed since the last application;
   2) Submit an amended Quality manual in accordance with 64808;
   3) Submit performance test sample results in compliance with 64810. If performance test sample(s) do not exist, then submit data and documents showing the following
      A) The results of the initial demonstration of capability if the addition(s) are Field(s) of Accreditation consisting of analytical methods and analytes approved for regulatory use by state or federal agency.
   4) Submit fee payment in accordance with 64806
b) If amending accreditation by the removal of one or more Fields of Accreditation a laboratory shall:
   1) Submit a notice of intent to amend by removal and a list of Field(s) of Accreditation to be removed.
   2) Submit an amended Quality manual in accordance with
   3) The effective date with regards to accreditation is the date of the laboratory's notice to ELAP.

§64802.20 Acceptance of Another State or Federal Government Agency's Accreditation

a) A laboratory may submit an accreditation issued by another State or by a federal government agency and request accreditation if any of the following conditions exist
   1) ELAP grants recognition for a certificate issued by:
      A) An issuing agency recognized by The NELAC Institute as an Accrediting Body; or
      B) An issuing agency of the federal Department of Defense or Department of Energy. This includes any third-party accrediting bodies employed by either agency.
b) The other agency's accreditation must be submitted with an application per section 64804 along with the results of all applicable PT results and the onsite assessment findings issued by the accrediting agency.
c) The requested Field(s) of Accreditation must match those cited on the other agency's accreditation.
d) Per H&SC 100845.(a) any issued ELAP accreditation expires 24 months from the date of issue. If during that period, the laboratory is to report to ELAP within 15 days of the event if any of the following occur.
   1) The issuing agency renews the certificate. The laboratory is to provide a copy and any attached lists of Fields of Accreditation.
   2) The issuing agency denies; revokes; or suspends the certificate. The laboratory is to provide details of the reasons and the effective date. If the certificate is suspended,

then the period of suspension.

e) When renewing ELAP accreditation, the laboratory is to comply with the renewal process as stated in section 64802.10.
f) ELAP retains authority under H&SC 100865.(a) to submit PT samples or conduct an onsite assessment of the laboratory. The laboratory shall pay all applicable fees per section 64806.

§64802.25 Changes in laboratory name or location; structural alteration; or adding mobile or auxiliary facilities

a) During the 24-month duration of accreditation the laboratory will provide written notification to ELAP within 30 days if any of the following occurs:
   1) Change in laboratory name. The laboratory is to report the old and new names. The change cannot be as a result of a change in ownership. Name change via change in ownership is to comply with section 64816
   2) Change in physical location or structural alterations or
   3) Addition of auxiliary or mobile facility(ies).
   4) The written notice shall include applicable fees per section 64806.
b) Conditions defining an auxiliary facility are as follows:
   1) Operated by the owner of a laboratory for the purpose of providing additional capacity, or to reduce or eliminate sample contamination; and
   2) Performs analyses in one or more of the same Field(s) of Accreditation listed under the accreditation; and
   3) Under the supervision of the Laboratory Director as the laboratory to which it is auxiliary; and

c) ELAP under authority of H&SC 100865(a) may submit PT samples or conduct onsite assessments of the laboratory for any change in location, structural alteration or addition of auxiliary or mobile facility(ies).

Article 3. Application Packages

§64804 Application Packages

a) A laboratory applying for initial accreditation shall submit an application package with the following information
   1) Laboratory Name
   2) Laboratory location address
   3) Contact information including at least a mailing address; phone number and e-mail address for the person designated the Laboratory Director. The laboratory may supply contact information for other persons within the laboratory
   4) Name of person(s) identified as Technical Manager(s) and information supporting meeting the qualifications in section 64814. This position may be filled by the Laboratory Director as long as that person meets the requirements of section 64814.
   5) Name of the person identified as the Quality Manager. This position may be filled by a Technical Manager or the Laboratory Director.
   6) A complete list of Field(s) of Accreditation sought for accreditation
   7) The application must be signed by an Owner or an Owner's agent
   8) A Quality manual in accordance with 64808

Article 4. Accreditation Fees

§64806. Accreditation Fees (fees are place-holders only)

a) Laboratories shall pay the following fees when required by this standard
   1) Application fee for initial applications required by 64802.05: $XXX
   2) Application fee for filings required by 64802.10, 64802.15, or 64802.20: $XXX
   3) Application fee for filings required by 64802.25: $XXX
   4) Annual fee as required by H&SC 100860.1.(a): $XXX
   5) Onsite assessments, whether conducted by ELAP or an approved third-party will be billed for the following costs:
      A) Travel including air/rail; rental car; hotel at receipted costs
      B) Mileage at federal rate for the year the on-site conducted
      C) Up to 24 hours at the prevailing hourly charge for on-site assessment preparation
      D) The hours taken to conduct the on-site assessment
      E) Up to 16 hours to submit the final assessment report and evaluate the laboratory's submission

Article 5. Quality System Standards

§64808.00 Quality System Standards

a) Laboratories seeking or holding accreditation shall comply with the quality management system as identified in b) through i)
b) Each laboratory shall have a quality manual formatted and with contents as follows
   1) TNI, 2016, Rev. 2.1 Volume 1, Module 2, Section 4.2.8.3 a) through l), except e), and g);
   2) TNI 2016, Rev. 2.1 Volume 1, Module 2, section 4.2.8.4 a) through r).
   3) The laboratory must have a procedure in the quality manual and shall conduct internal audits in compliance with TNI 2016, Rev. 2.1 Volume 1, Module 2, section 4.14. The audits may be scheduled as necessary however, shall be completed by the end of each 12-month portion of accreditation.
c) Laboratories are to adopt all quality assurance and quality control procedures; and criteria as specified in appropriate federal or state regulation; or in the federal or state regulatory approved methods the laboratory is accredited for.
d) Incorporate the contents of TNI, 2016, Rev. 2.1, Volume 1, Modules 3 through 7 (as appropriate for the test method) only where the test method or federal, state, and local regulation are silent on the requirement. In all cases requirements found in regulation or methods approved by regulation supersede requirements found in TNI, 2016, Rev. 2.1 Modules 3 through 7.
e) The laboratory shall have Standard Operating Procedures (SOP) for all the analytical methods the laboratory is seeking or holding accreditation. The format for all analytical SOPs shall contain discussion on the topics found in TNI, 2016, Rev. 2.1, Volume 1 Module 2, section 4.2.8.5.f).i) through xxiii. The SOP shall designate if any topic is not applicable to the method.
f) The laboratory is to employ the requirements in TNI, 2016, Rev. 2.1 Volume 1, Module 2 sections 5.5; 5.8; and 5.9. The quality management system shall include the requirements found in TNI, 2016, Rev. 2.1 Volume 1, Module 2, section 5.7 if any laboratory staff conduct sampling, even if on a temporary basis.
g) The laboratory shall incorporate data integrity training per TNI 2016, Rev. 2.1 Volume 1, Module 2, section 5.2.7. The training shall include ethics and ethical behavior training. The frequency shall be at least equal to the requirement in section 64812.00.(c).
h) Any section within the TNI, 2016, Rev. 2.1 standard that relates to the operation of a calibration laboratory are not applicable to this standard.
i) All items that are Notes in the TNI, 2016, Rev. 2.1 standard are not applicable or enforceable per the statement at the end of Volume 1, Module 2, section 1.2.

§64808.05 Onsite assessments of 64808.00

a) All on-site assessments will be conducted in accordance with the requirements found in General Requirements for Accreditation Bodies Accrediting Environmental Laboratories 2009 Rev. 0.1 V2M3 Section 6.

b) As allowed by Health and Safety Code section 100837, the laboratory may select a

recognized third-party assessment organization. To be recognized, any third-party assessment organization shall possess any of the following

1) Training certificates for Basic Assessor as issued by TNI. The possession of a training certificate for TNI 2016, Rev. 2.1, Volume 1, Module 6 is required to assess under this module.
2) An approved assessor for a non-governmental accrediting body with evidence of training in ISO 17025:2005 or ISO 17025-2017.
3) An approved assessor for the federal Department of Defense or Department of Energy.
4) An approved assessor accepted by ELAP.

c) All assessments must be conducted within the 12th month to 20th month of accreditation.

§64808.10 Service Transparency

a) Within three (3) years of the adoption of these regulations, ELAP shall conform to the standards found in TNI 2016, Rev. 2.0 (a.k.a. TNI 2009, Rev. 0.1). ELAP may opt to conform to the standards found in ISO 17011:2017. If it does, then it shall also undergo assessment against the standard by a competent assessment organization.

Article 6. PT Study Requirements

§64810. PT Study Requirements.

a) Laboratories seeking or holding ELAP accreditation shall analyze PT samples applicable for the Field(s) of Accreditation cited in the application or on the accreditation.
b) All laboratories shall comply with H&SC 100870.(d) including use of providers meeting current TNI standards; payment of any fees charges; and the release of study results directly to ELAP.
c) The following table cross-references Fields of Accreditation matrices with Fields of Proficiency Testing matrices

Field of Proficiency Testing Matrix	Field of Accreditation Matrix
Drinking Water	Drinking Water
Non-Potable Water	Aqueous and Saline/Estuarine
Solids	Solids
Oil and Solvent	Non-Aqueous Liquid

d) All laboratories shall select PT samples that match the method/technology-analyte within the matrix cross reference above for which the laboratory is seeking or hold accreditation
e) PT results submitted for initial accreditation under 64802.05 above shall have a closing date of the study more than 3 months prior to the application date.
f) Laboratories accredited under ELAP accreditation shall meet the following.
    1) Accredited laboratories shall analyze PT samples within the first 12 months from the date of issue of the accreditation or renewed accreditation and achieve acceptable results for all PT Fields of Proficiency Testing analyzed. If any result is marked unacceptable then the laboratory shall obtain samples from the next available PT sample study set. If any result from the second set is also unacceptable then the laboratory is subject to revocation per H&SC 100850.(b).(1).
    2) Accredited laboratories shall within the second 12 months of accreditation but before 1 month from the stated expiration date analyze and achieve acceptable results for all PT Fields of Proficiency analyzed. If a second set is necessary, it must be completed and results available prior to 1 month from the stated expiration date. A failure to achieve acceptable results in the second set or a failure to provide results prior to 1 month from the expiration date shall be grounds for denial of that Field(s) of Accreditation per H&SC 100850.(b).(1)

Article 7. Laboratory Personnel Requirements

§64812.00 Personnel Training

a) Laboratories shall establish a training program for all personnel and assure that those designated as Technical Manager and Quality Manager meet any educational, experience; or certificate requirements for each position as found in 6481205 or 64812.10 respectively.
b) The training program shall cover the test methods for which the laboratory is accredited. It may be a combination of internal or external provided programs and may include those taken in order to maintain any certificates.
c) The training program shall include a data integrity component meeting the requirements of TNI 2016, Rev. 2.1, Volume 1, Module 2, section 5.2.7. The training shall be given annually to all laboratory personnel. As evidence of the training, all laboratory personnel shall sign an agreement to conform to the laboratory's data integrity procedures and ethics policy.
d) The laboratory shall include in its training program defined Demonstrations of Capability as required by the federal or state regulatory approved method. If the method is silent then the requirements of section 1.6.1 as found in TNI 2016, Rev. 2.1, Volume 1, Modules 3 through 7 (as appropriate for the test method) shall be followed.

§64812.05 Technical Manager Qualifications

a) All laboratories shall identify at least one person as a Technical Manager. As allowed in 64800.(a).(11), the Laboratory Director is identified as a Technical Manager.
b) Those person(s) identified as Technical Manager(s) shall comply with the following educational and experience requirements, except water or wastewater treatment plant laboratories seeking or holding accreditation for any Field of Accreditation associated with analyses required under Section 4025 of the Health and Safety Code, or Section 13176 of the Water Code.
c) Possess a Baccalaureate degree in chemistry, biochemistry; biology; microbiology; natural sciences; physical sciences; environmental science; sanitary engineering; or chemical engineering.
d) Have three (3) years' experience in the analysis of samples in an environmental laboratory prior to be designated as a Technical Manager.
    1) Possess a Baccalaureate degree in chemistry, biochemistry; biology; microbiology; natural sciences; physical sciences; environmental science; sanitary engineering; or chemical engineering.
    2) Have three (3) years' experience in the analysis of samples in an environmental laboratory prior to be designated as a Technical Manager.
        A) Possession of a Master's degree in any of the fields cited in (b).(1) above may be substituted for one (1) year of experience.
        B) Possess of a Doctoral degree in any of the fields cited in (b).(1) above may be substituted for two (2) years of experience.
e) Excepted laboratories may fulfill the requirements for Technical Manager by the Technical Manager possessing a Laboratory Analyst or Water Quality Analyst Certificate from the

California Water Environment Association (CWEA) or the California-Nevada Section of the American Water Works Association (CA-NV/AWWA). The minimum grade of the above certificate acceptable shall be based on the Field(s) of Accreditation as noted in the conversion table set out below:

Field of Accreditation Method/Technology under Matrices Drinking Water and Non-Potable Water	CA-NV AWWA water quality analyst certificate	CWEA laboratory analyst certificate
All microbiological methods/All technologies **All solids methods/all technologies** **Biochemical Oxygen Demand (BOD) including the carbonaceous version (cBOD)**	I	I
All methods/titrimetric technologies **All methods/specific ion electrode technologies** **All methods/colorimetric technologies**	II	II
All methods/ion chromatography **All methods/flame atomic absorption** **All methods/graphite furnace atomic absorption**	III	III
All methods/all chromatography technologies including those using mass detectors **All methods/ICP** **All methods/ICPMS**	IV	IV

§64812.10 Quality Manager Qualifications

a) Laboratories shall identify a person as the Quality Manager. As allowed under 64800.(a).(11), the Quality Manager may be the same person identified as the Technical Manager and/or the Laboratory Director.
b) The Quality Manager is to possess knowledge of the quality systems associated with the test methods for which the laboratory is accredited related to TNI 2016, Rev. 2.1, Volume 1, Module 2, section 4.1.7.1. The evidence shall be either training received or experience with the test method(s).

§64812.15 Changes in Persons Identified as Technical Manager

a) Laboratories shall notify ELAP if there is a permanent change in Technical Manager. The notification shall include the identity of the new person; the effective date of the change; and evidence of their compliance with any qualification requirements.

b) If the replacement will take longer than 90 days due to required hiring procedures then the laboratory shall notify ELAP in writing with a projected timeframe for hiring the replacement.
c) The laboratory shall notify ELAP In cases where the Technical Manager is to be absent for more than 60 days.

Article 8. Notification and Reporting

§64814. Notification and Reporting.

a) Laboratories accredited for Fields of Accreditation where the Matrix is Drinking Water shall conform to the following reporting and notification requirements.
b) Laboratories reporting bacterial quality results as required by Title 22, California Code of Regulations, Section 64423.1 shall submit a bacterial monitoring report including information required in Title 22, California Code of Regulations, Sections 64423.1(c)(2) and (c)(3) directly to the Department of Drinking Water.
c) The laboratory shall notify a water supplier's designated contact person as soon as possible, but within 24 hours, and record the method and time of notification or attempted notification, whenever any of the following occur:
    1) The presence of total coliforms, fecal coliforms, or Escherichia coli (E. coli) is confirmed.
    2) A bacterial sample is invalidated due to an interference as defined in Title 22, California Code of Regulations, Section 64425(b).
    3) A nitrate sample exceeds the MCL.
d) If the laboratory is unable to make direct contact with the supplier's designated contact person within 24 hours, pursuant to subparagraphs (2)(A) or (C), the laboratory shall immediately notify the Department of Drinking Water and provide a written record of the time and method of attempted contacts.
e) All analytical results conducted pursuant to Title 22, California Code of Regulations, Chapter 15, Domestic Water Quality and Monitoring, shall be reported directly to the Department of Drinking Water electronically using the Electronic Deliverable Format as defined in The Electronic Deliverable Format [EDF] Version current at the time reporting is made and Data Dictionary concurrent with that version, by the 10th day of the month following the month in which the analyses were completed.
f) Whenever a laboratory is requested by a water supplier, pursuant to Title 22, California Code of Regulations, Section 64425(a)(2), to submit evidence invalidating a sample due to laboratory error, the laboratory shall provide the supplier with information which shall include:
    1) A letter from the Laboratory Director to the water supplier agreeing to the invalidation request by reason of laboratory accident or error;
    2) complete sample identification, laboratory sample log number (if used), date and time of collection, date and time of receipt by the laboratory, date and time of analysis for the sample(s) in question;
    3) complete description of the error alleged to have invalidated the result(s);
    4) copies of all analytical, operating, and quality assurance records pertaining to the incident in question; and
    5) any observations noted by laboratory personnel when receiving and analyzing the sample(s) in question.
g) In any arrangements between laboratories involving the transfer of samples, or portions of samples, the laboratory issuing the report of analyses shall include the original of any report(s) prepared by all other laboratories who are party to the agreement.

Article 9. Trade Secrets

§64816. Trade Secrets.

1. If a laboratory identifies information provided to the ELAP as a trade secret, ELAP shall not release such information unless:
    a. The release is authorized under state or federal law; and
    b. ELAP has notified the laboratory of the impending release. Such notification shall be at least ten days prior to releasing any information identified as a trade secret, stating the name of the party requesting the information, the reason for the request, the authority to release this information, and the date the information will be released.

Article 10. Sale or Transfer of Ownership of a Laboratory

§64818. Sale or Transfer of Ownership

1) A certificate shall be voided by operation of law if one or more of the following occurs.
   a) An original Owner fails to notify the ELAP, in writing, within 15 days after a change in ownership.
   b) A new Owner relocates the laboratory within 90 days of assuming ownership.
   c) If more than half the number of laboratory persons either quit or are terminated and replaced by a new Owner within 90 days of assuming ownership.
   d) If a new Owner submits an application to alter the laboratory's certificate as issued to the prior Owner by the addition of any Subgroup within any Field of Testing.
2) A new Owner of a laboratory shall notify the ELAP, in writing, within 15 days after the sale or transfer of ownership and provide, at minimum, the following information.
   a) The name(s) of the new Owner(s).
   b) The date of sale or transfer of ownership.
   c) The name(s), education and experience, as specified in Section 64812.05.(b); or voluntary laboratory certificate grade as specified in Section 64812.05.(c), of the person(s) designated as Technical Manager(s).
   d) The name of the person designated as Quality Manager.
   e) The name(s) of all Technical Manager(s) and/or Quality Manager who quit, or were terminated and replaced.
   f) A statement that there will be no changes in laboratory location, or in the certificate issued to the prior Owner(s) within 90 days of assuming ownership.
   g) A statement that all equipment, method, and quality assurance practices will not change within 90 days of assuming ownership.
   h) The notice shall be signed by one or more of the new Owner(s), or their Agents.
3) New Owners that comply with the provisions of (b) above shall have use of the certificate issued to the prior Owner for a period of ninety days commencing with the date of the ELAP's notice of receipt of the information supplied by the new Owner.
   a) The certificate number and the laboratory name appearing on the certificate shall remain the same.
   b) The new Owner shall display, and provide a copy with all data reports, the ELAP's notice recognizing the sale or transfer of ownership.
4) To obtain the use of the certificate to its original expiration date, the new Owner shall request such use in writing, and the laboratory shall be subjected to, and pass the following, within the 90 days use period granted by the ELAP.
   a) An onsite assessment to determine compliance with 64808; and
   b) Successful completion of PT samples in accordance with 64810.

LUNCH BREAK

Resume at 1:15 PM

ELTAC SUBCOMMITTEE ON ALTERNATIVE QMS

Agenda Item #6

2018 DRAFT TOXICITY PROVISIONS

Karen Mogus, Division of Water Quality

Agenda Item #7

2018 Draft Toxicity Provisions

For the Water Quality Control Plan for
Inland Surface Waters, Enclosed Bays, and Estuaries of California

Karen Mogus, Deputy Director
Division of Water Quality

State Water Resources Control Board
April 17, 2019

- Goals
- Description of the Provisions
- Timeline
- Contact Info

Goals

1. Adopt consistent, statewide numeric water quality objectives for acute and chronic toxicity
2. Adopt a program of implementation
3. Create a consistent, yet flexible framework for monitoring toxicity and laboratory analysis
4. Incorporate a statewide statistical approach to analyze test results that will provide a transparent determination of toxicity

Numeric Water Quality Objectives for Aquatic Toxicity

Numeric Chronic Aquatic Toxicity Objective

Null Hypothesis (H_0):

Mean Response (ambient receiving water) ≤ 0.75 x Mean Response (control)

Numeric Acute Aquatic Toxicity Objective

Null Hypothesis (H_0):

Mean Response (ambient receiving water) ≤ 0.80 x Mean Response (control)

Aquatic Toxicity Test Methods

- Toxicity tests shall be conducted using one or more test species in Table 1 of the Toxicity Provisions
- Methods shall follow EPA method manuals

Fathead Minnow

Green Algae (*Selenastrum*)

Water flea (*Ceriodaphnia*)

Public Comments: *Ceriodaphnia* Reproduction Test

- High inherent and within-test variability
- Incorrect determinations of toxicity in non-toxic samples
- Sensitive test organism
- Not reliable with the Test of Significant Toxicity statistical approach

Test of Significant Toxicity

- A statistical hypothesis test
- Data analysis approach, not a change to test methods
- Tests the hypothesis:
  - Does the sample and the control differ by a biologically significant amount?
- Produces a clear pass/fail result
- Provides greater confidence
- Incorporates the regulatory management decision
- Developed by the U.S. EPA
- Validity of the TST was evaluated by the U.S. EPA and the California TST Test Drive

Program of Implementation

- Non-Stormwater NPDES Dischargers
  - **Species Sensitivity Screening**
  - Reasonable Potential Analysis
  - **Routine Monitoring Frequency**
  - **Effluent Limitations**
  - **Toxicity Reduction Evaluation**
  - Additional Considerations

- Storm Water and Nonpoint Source Dischargers

Species Sensitivity Screening

- Screening conducted as follows:
  - Chronic Testing – at least one vertebrate, one invertebrate, and one aquatic plant species
  - Acute Testing – at least one vertebrate and one invertebrate species
- Four sets of tests must be conducted over one year (or applicable discharge season)
- Required either prior to issuance of permit or within 18 months after first issuance
- No less than once every 10 years
- Species with highest percent effect at the Instream Waste Concentration is generally selected as the most sensitive species

Routine Monitoring Frequency

- **Chronic Toxicity** Routine Monitoring Frequency:

POTWs ≥ 5 MGD	Other NPDES Dischargers ≥ 5 MGD w/ RP	POTWs < 5 MGD w/ RP	Other NPDES Dischargers < 5 MGD w/ RP
Monthly	Monthly	Quarterly	Quarterly

- **Acute Toxicity** Routine Monitoring Frequency:
  - Determined by the Regional Water Boards
  - At a minimum, must be conducted annually

Chronic Toxicity Numeric Effluent Limitations

Chronic Toxicity Maximum Daily Effluent Limitation

No chronic toxicity test shall result in a "fail"*
at the IWC for the sub-lethal endpoint measured in the test
and a percent effect for the survival endpoint ≥ 50%

Or if no survival endpoint can be measured, then:

No chronic toxicity test shall result in a "fail"*
at the IWC for the sub-lethal endpoint measured in the test
and a percent effect for the sub-lethal endpoint ≥ 50%

Chronic Toxicity Monthly Median Effluent Limitation

*No more than one chronic toxicity test**
initiated in a calendar month
shall result in a "fail"
at the IWC for any endpoint

** Using the most sensitive species*

MMEL Compliance

Routine Monitoring Test	Compliance Test 1	Compliance Test 2	MMEL Violation?
Pass	NA	NA	No
Fail	Pass	Pass	No
Fail	Pass	Fail	Yes
Fail	Fail	NA	Yes

Questions for Laboratories

- Do you conduct wastewater treatment plant testing in compliance with NPDES permits?
- How long does it take to receive preliminary test results using the TST?
- How much notice do you need to initiate a chronic toxicity test?
- Do you have a contingency plan when you are unable to conduct a test due to constraints (limited capacity, control failure, test does not meet Test Acceptability Criteria)?
- Approximately what costs are associated with a chronic toxicity test?

Toxicity Reduction Evaluation

- A toxicity reduction evaluation (TRE) is required when two violations of either effluent limitation occurs within a calendar month or in consecutive calendar months
- Routine monitoring shall continue during a TRE
- Regional Water Boards have discretion to require a TRE if other information (i.e., fish kills) indicates toxicity

Storm Water & Nonpoint Source Dischargers

- Water Boards have discretion to require toxicity testing using any species
- If requiring species from Table 1, the TST statistical approach must be used
- Any future requirements for testing with the species in Table 1 also will be required to use the TST statistical approach

Timeline

Board Meeting Workshop	July 2, 2019
Board Consideration of Adoption	September 17, 2019

Contacts

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Rebecca Fitzgerald, Manager, Water Quality Standards and Assessment Section
Division of Water Quality, State Water Resources Control Board
Rebecca.Fitzgerald@waterboards.ca.gov, (916) 341-5775

Documents & Additional Information Available at:
https://www.waterboards.ca.gov/water_issues/programs/state_implementation_policy/tx_ass_cntrl.html

PFAS PHASED INVESTIGATION APPROACH

Annalisa Kihara, Division of Water Quality

Agenda Item #8





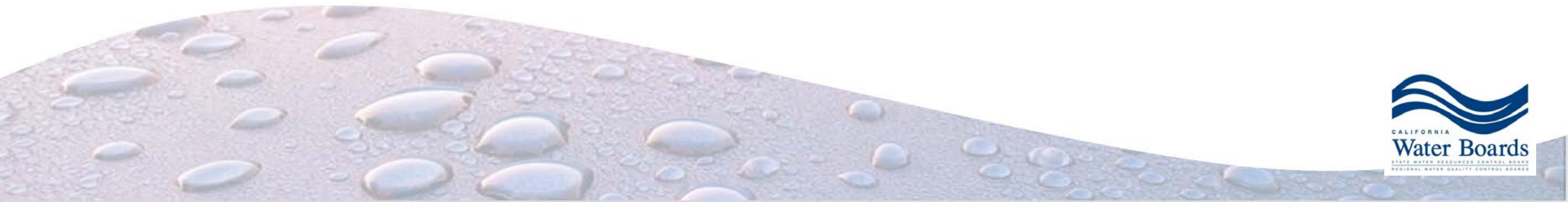
Water Boards - DWQ
PFAS Phased Investigation Approach

Annalisa Kihara

Supervising Water Resource Control Engineer, Division of Water Quality

Scott Coffin, PhD

Environmental Scientist, Division of Water Quality



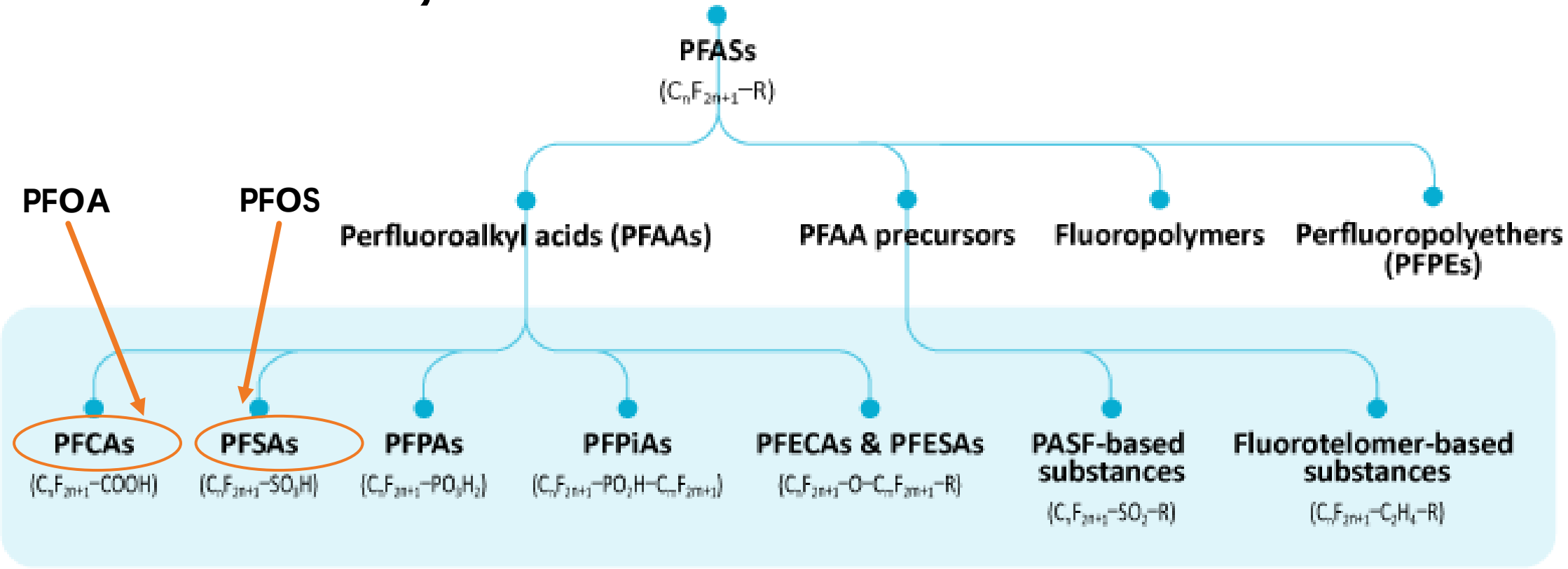
PFAS Background and Use

- **Per- and Polyflouroalkyl Substances (PFAS)**:
  - Group of man-made chemicals resistant to heat, water, and oil
  - Manufacturing started in the 1940s and are still produced today
  - **Perfluorooctanoic acid (PFOA)** and **perfluorooctanesulfonic acid (PFOS)** included in >3,000 compound family

One of the strongest bonds in chemistry, leads to **environmental persistence**

PFAS Background and Use

- **There are >3,000 PFAS**:



Wang et al. (2017)

PFAS Background and Use

- **Used in industrial and consumer products:**
  - Carpets & rugs,
  - Water-proof clothing,
  - Upholstery,
  - Food paper wrappings,
  - Cleaning products,
  - Metal plating (e.g., cookware),
  - Fire-fighting foams,

PFAS Background and Use

- **Perfluoroalkyl acids (PFAAs) are hazardous to humans:**
  - Carcinogenicity *(kidney and testicular cancers)*
  - Cardiovascular toxicity *(increased serum cholesterol)*
  - Endocrine toxicity *(thyroid disease)*
  - Immunotoxicity *(ulcerative colitis, immune dysregulation)*
  - Reproductive toxicity *(pregnancy-induced hypertension)*

March 6, 2019
Water Board Informational Item

- **Panel Presentations**:
  - U.S. EPA
  - Department of Defense
  - Environmental Advocacy
  - Office of Environmental Health Hazard Assessment
  - Department of Toxic Substances Control
- **Water Board's Phased PFAS Investigation Plan**
- **Public Comment**

PFAS Phased Investigation Approach
Airport Phase I Sampling

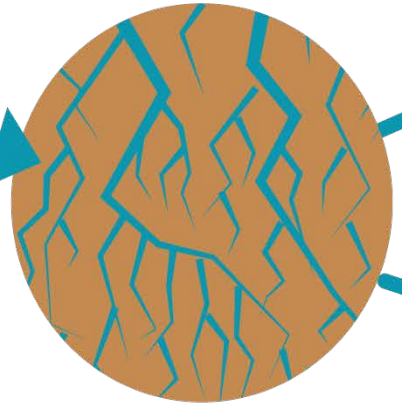
- ***27* Airports with training/fire response sites**
  - California Water Code 13267 Investigative Orders sent on March 20, 2019

- **Drinking water wells (2 mile radius)**
  - California Health and Safety Code 116400 Orders

PFAS Phased Investigation Approach
Landfills Phase I Sampling

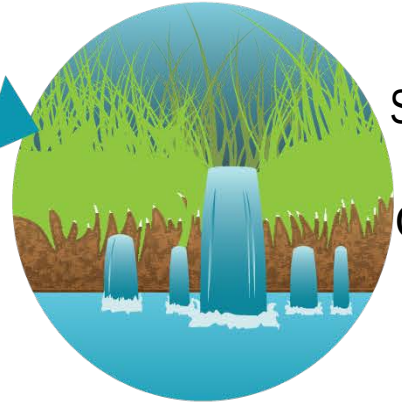
RAINFALL

CARPET
WASTE
IN LANDFILL



LEACHATE

WASTEWATER
TREATMENT
PLANT

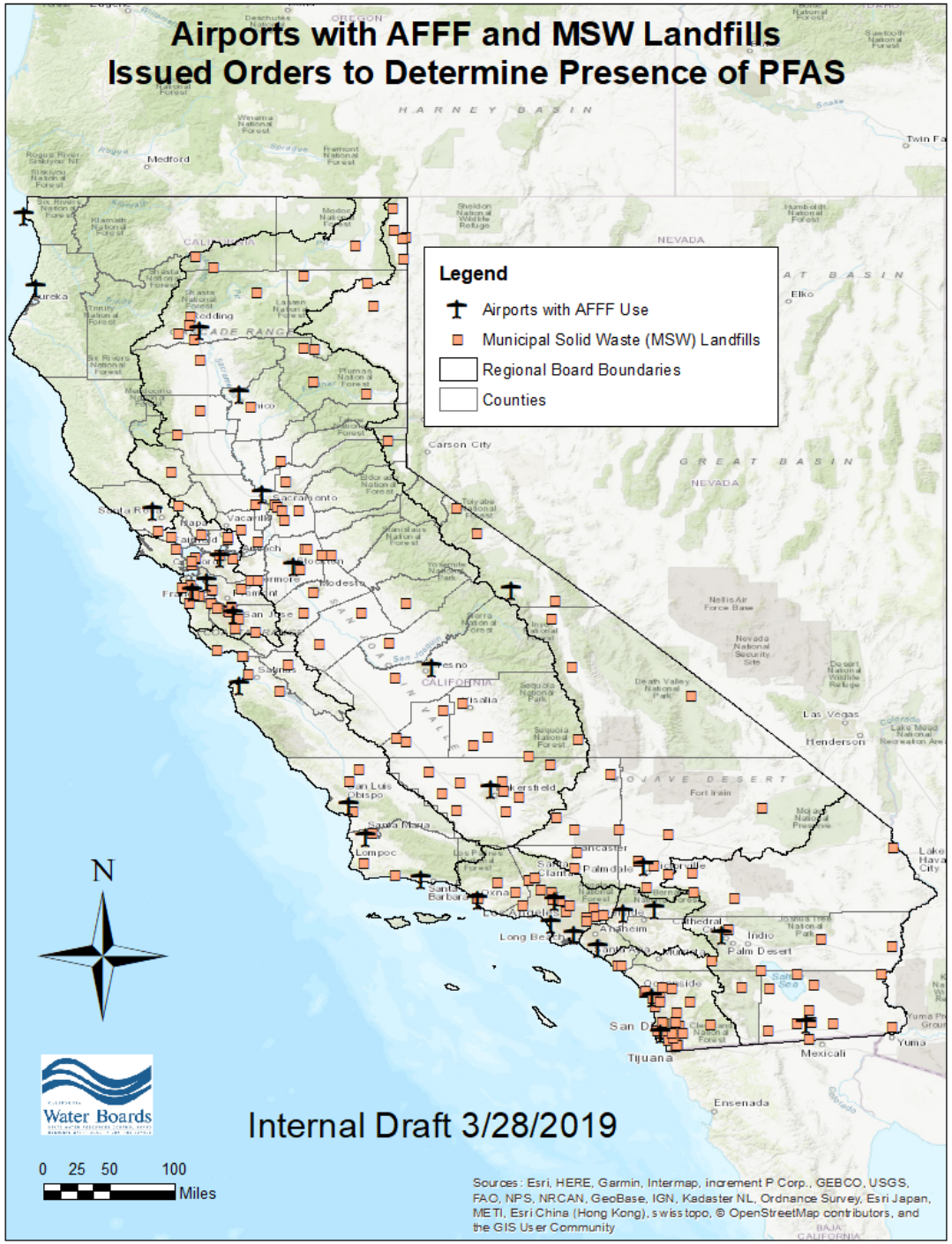


SURFACE WATER
OR
GROUNDWATER

In California, 75% (257 million pounds) of the carpet discarded in 2016 was landfilled

PFAS Phased Investigation Approach
Landfills Phase I Sampling

- ***194* Municipal solid waste (MSW) landfills**
  - CA Water Code 13267 Investigative Orders sent March 20, 2019
- **Drinking water wells (1 mile radius)**
  - California Health and Safety Code 116400 Orders



- ***Map of:***
  - **MSW landfills**
  - **Airports**

CALIFORNIA Water Boards

Laboratory Analyses

	Analysis Compliant w/ DoD QSM
Release Year:	**2017**
Matrices:	**GW, EF, WW, S, SE, SL**
Total PFAS Compounds Analyzed	**23-38**
Number of labs accredited by DOD ELAP	**16**
Number of labs accredited by CA ELAP	

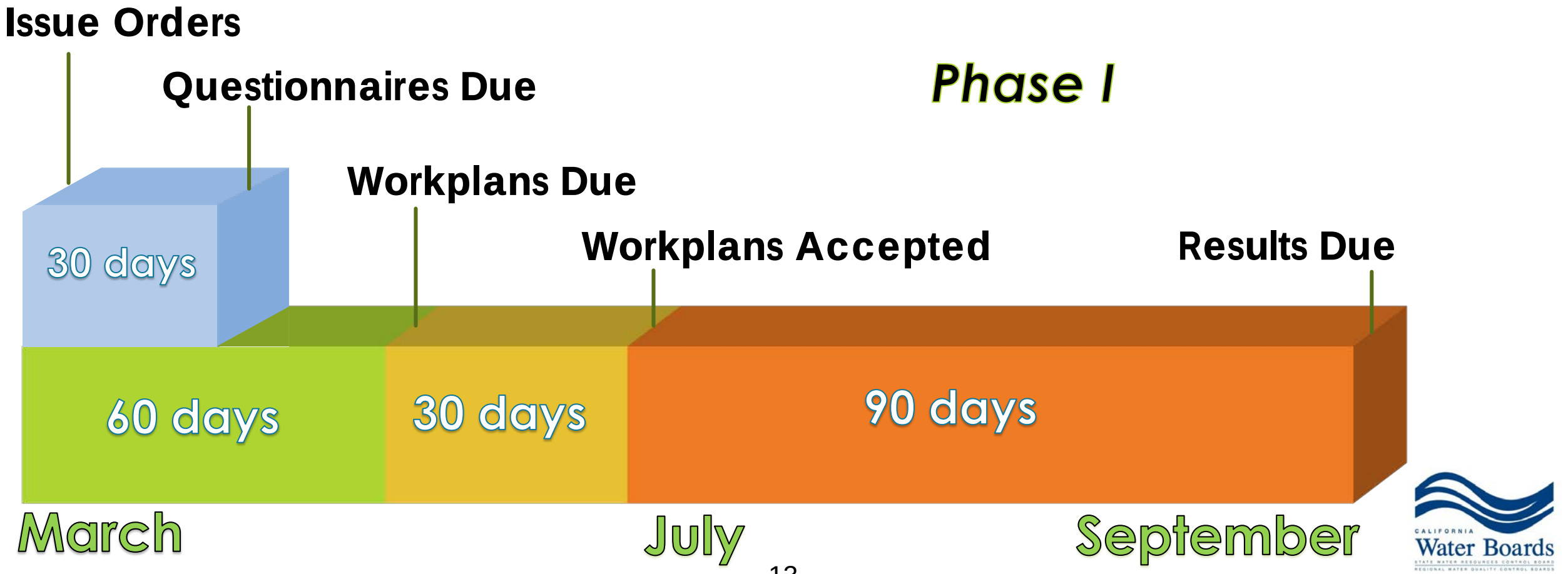
DW=Drinking Water **GW**=Groundwater **EF**=Effluent **WW**=Wastewater **S**=Soil **SE**=Sediment **SL**=Sludge

PFAS Phased Investigation Approach
Phase II & III Sampling

- **Investigations at:**
  - Industrial facilities
  - Refineries, bulk terminals, & non-airport fire training areas
  - 2017-2018 urban wildfire areas
  - Wastewater treatment & pre-treatment plants
  - Domestic wells

PFAS Phased Investigation: Timeline

- Each Investigation phase ~6 months
- Phases II and III to Investigation begin summer/fall 2019



Questions/Comments

Email: PFAS@waterboards.ca.gov

Website: waterboards.ca.gov/pfas/

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Scott Coffin, PhD
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NEW ANALYTICAL METHOD PHASING

Betsy Lichti, Division of Drinking Water

Agenda Item #9

NEW ANALYTICAL METHOD PHASING

ELTAC

April 17, 2019

BETSY LICHTI, PE, CHIEF
QUALITY ASSURANCE SECTION
DIVISION OF DRINKING WATER (DDW)

CALIFORNIA
Water Boards
STATE WATER RESOURCES CONTROL BOARD
REGIONAL WATER QUALITY CONTROL BOARDS

PFAS ANALYTICAL METHODS FOR DRINKING WATER

- DDW accreditation requests to ELAP

PFAS DW Method	Date Accreditation Request	Number of Analytes
EPA Method 537 Rev 1.1	July 2018	14
EPA Method 537.1	January 2019	18

- Additional EPA method under development:
  - Specific to short chain PFAS
  - Proposed to be published Summer 2019
  - Includes 25 PFAS analytes

DDW will evaluate and make a request to ELAP for accreditation if appropriate for data quality objectives

DDW BUSINESS RULE FOR PHASING IN NEW METHODS

- DDW QAS to decide on appropriate methods to meet data quality objectives
- Methods may be phased out as new/improved methods are available
- On request, ELAP will update the FOT to remove the old method and add the new method, offering accreditation under the new method
- Labs accredited for an older method must seek to renew with the new method when accreditation is expiring (generally 2 years) or sooner
  - DDW will continue to accept results under the old method until accreditation renewal
- Labs seeking NEW accreditation for an analyte must do so under the current method(s) listed in the ELAP FOT

PFAS METHOD PHASING

- Currently accepting EPA Method 537 Rev 1.1 from the currently accredited laboratories (9 to 13 labs)
- All additional labs requesting PFAS accreditation must do so under EPA Method 537.1
- If/When EPA Method 8328 is validated and published, DDW will consider data quality and analytes included to establish which methods(s) we will accept.
- If EPA 537.1 is phased out, DDW will adhere to the business rule noted previously
  - Labs can retain accreditation and use the old method until accreditation renewal, at which time they must seek accreditation under the current method(s) acceptable to DDW

Questions?

Contact Information:

Betsy Lichti
Betsy.Lichti@waterboards.ca.gov
(916) 322-9598

NON-POINT SOURCE AQUATIC SCREENING AND MONITORING

Daniel Whitley, Central Valley Regional Water Quality Control Board

Agenda Item #10

Central Valley Regional Water Quality Control Board

Non-Point Source Aquatic Screening and Monitoring

Status and Needs

Central Valley Water Board (Region 5)

- Approximately **20 million acres** Forested Lands
- **33** major watersheds (Upper Sacramento to Kern River)
- **Pesticides**
  - Cannabis Production (legal and illegal)
  - Industrial Forestry
  - Rights-of-Way
  - Transmission Line Corridors
  - Post-fire discharges

NPS discharges episodic and low level

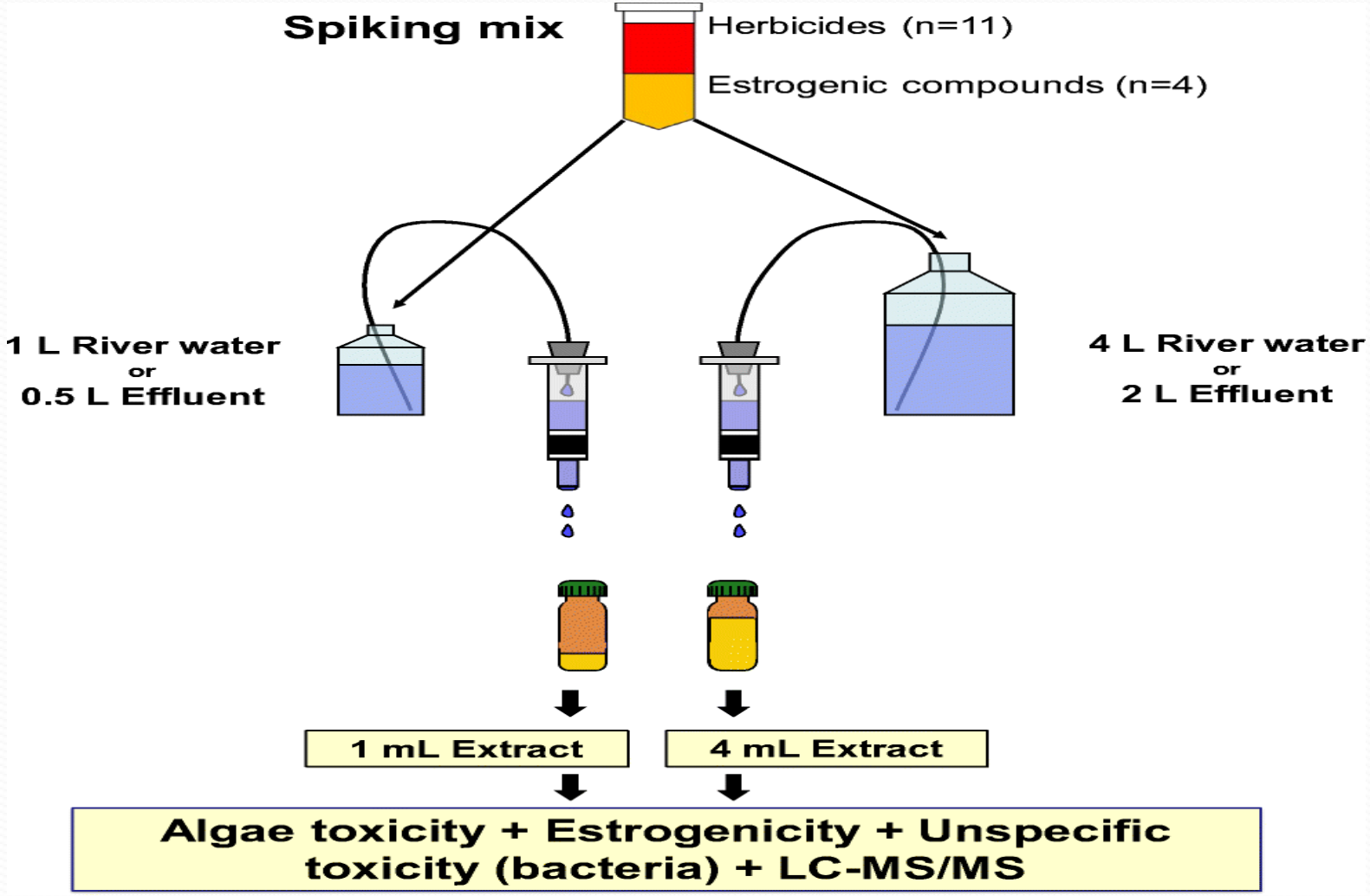
Central Valley Water Board – USGS Collaboration

- Dr. Michelle Hladik (Research Chemist)
  - Organic Chemistry Research Laboratory – USGS Pesticide Fate Research Group Sacramento (CSUS)

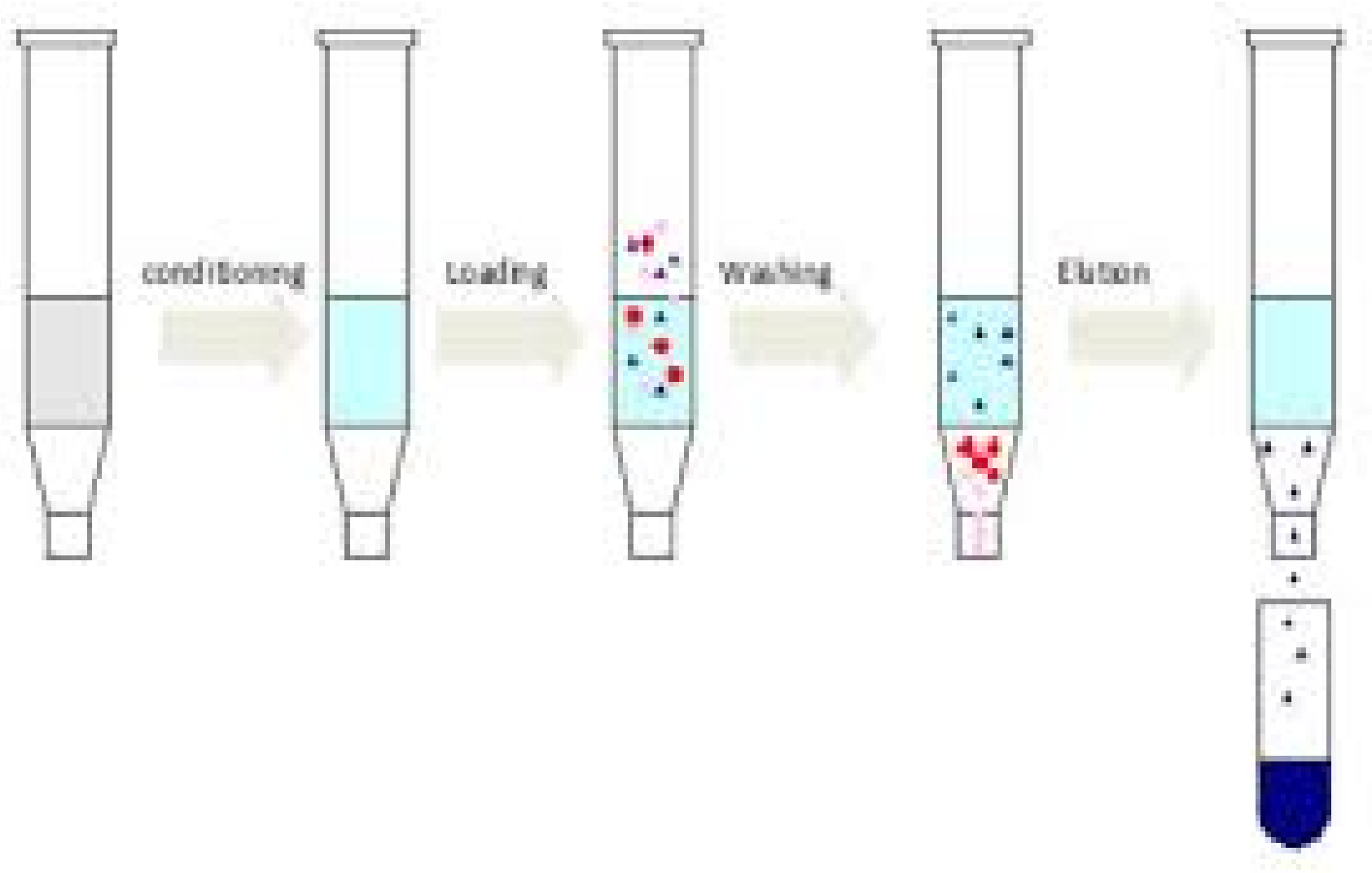
- Solid-Phase Extraction (SPE) media
- Aquatic Passive Samplers

Chemcatcher and SPE Disks

EPA Method 3535A (SPE Disc processing)

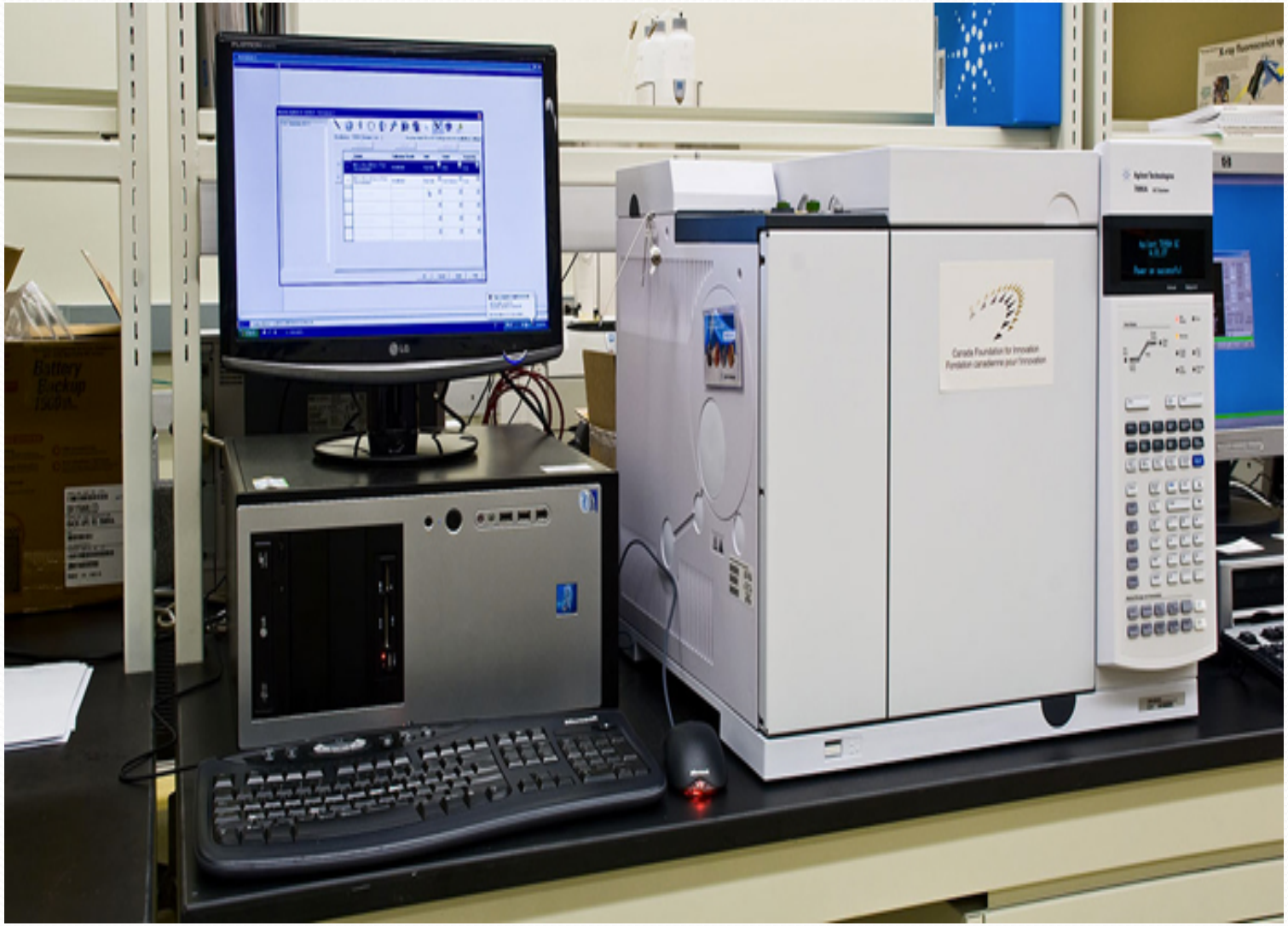


SPE Disc processing



USGS Methodology

GC/MS and LC-MS/MS optimized for the simultaneous analysis for 135 pesticides and pesticide degradates.



Screening & Monitoring

- Deer and Little Cow Creek detections (***salmonids***)
  - *Chlorothalonil & *Trifluralin
- Post-fire detections of toxic fungicides/insecticides
  - **Asoxystrobin*, *Dithiopyr*, *Diuron*, **Fipronil*, *Fluopicolide*, *Hexazinone*, **Methoxyfenozide*, and *Napropamide*
- Battle Creek post-fire detections
  - *All pesticides reported as used (PUR)*

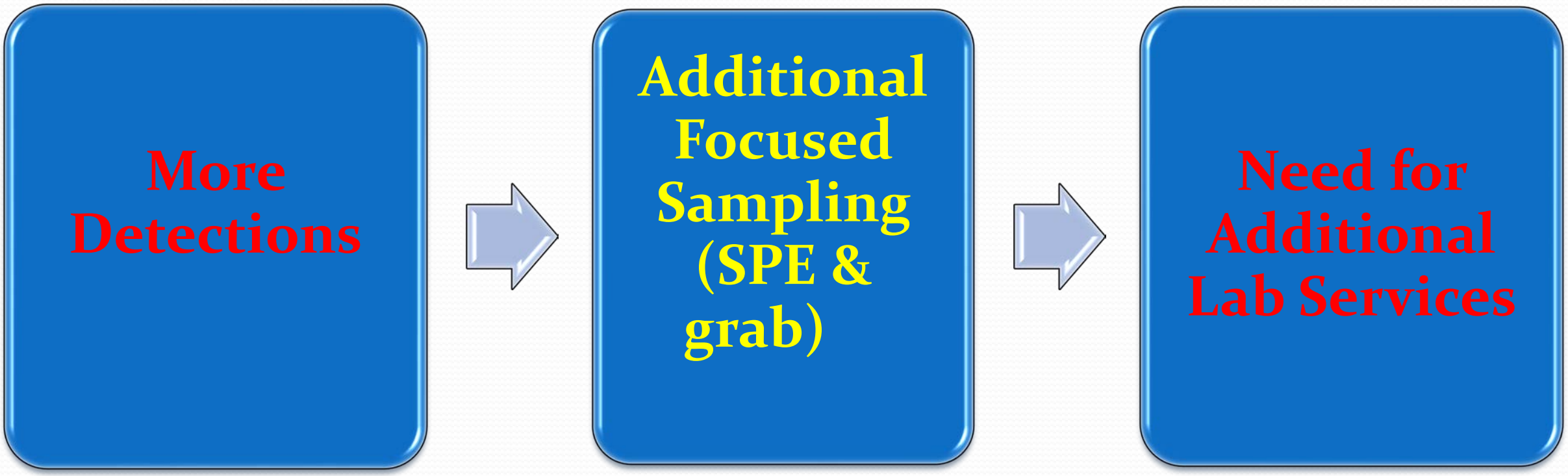
Water Boards Future Needs

- Lab Contract to include modified 3535A and USGS Methodology
- Significantly expand NPS screening and monitoring statewide
- Other Water Board Program use includes:
  - Cannabis Regulatory (R1, R5)
  - Irrigated Lands
  - SWB (SWAMP SPoT - statewide)

Statewide Use and Growth

- DDW
- CDFW
- DPR
- Local Municipalities
- Citizen Monitoring Groups
- RCDs
- USFS
- BLM
- NPS
- State Parks
- NMFS

Low detection limits and larger analyte list…



Questions

METHOD 3535A

SOLID-PHASE EXTRACTION (SPE)

SW-846 is not intended to be an analytical training manual. Therefore, method procedures are written based on the assumption that they will be performed by analysts who are formally trained in at least the basic principles of chemical analysis and in the use of the subject technology.

In addition, SW-846 methods, with the exception of required method use for the analysis of method-defined parameters, are intended to be guidance methods which contain general information on how to perform an analytical procedure or technique which a laboratory can use as a basic starting point for generating its own detailed Standard Operating Procedure (SOP), either for its own general use or for a specific project application. The performance data included in this method are for guidance purposes only, and are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

1.0 SCOPE AND APPLICATION

1.1 This method is a procedure for isolating target organic analytes from aqueous samples using solid-phase extraction (SPE) media. It describes conditions for extracting a variety of organic compounds from aqueous matrices that include groundwater, wastewater, and Toxicity Characteristic Leaching Procedure (TCLP, Method 1311) leachates. This method describes the use of disk extraction media for nine groups of analytes and the use of cartridge extraction media for two groups of analytes. Other solid-phase extraction media may be employed as described in Sec. 6.0. The extraction procedures are specific to the analytes of interest and vary by group of analytes and type of extraction media. The groups of analytes that have been evaluated thus far are listed below, along with the types of extraction media that have been evaluated and the determinative methods in which the corresponding performance data can be found.

Analyte Group	Extraction Media Type	Determinative Method
Phthalate esters	Disks	8061
Organochlorine pesticides	Disks	8081
Polychlorinated biphenyls (PCBs)	Disks	8082
Organophosphorus pesticides	Disks	8141
Nitroaromatics and nitramines	Disks and Cartridges	8330
Explosives*	Disks and Cartridges	8095
TCLP leachates containing organochlorine pesticides	Disks	8081
TCLP leachates containing semivolatiles	Disks	8270
TCLP leachates containing phenoxyacid herbicides	Disks	8321

* Includes the nitroaromatics, nitramines, and nitrate esters listed in Method 8095

1.2 This technique may also be applicable to other semivolatile or extractable compounds. It may also be used for the extraction of additional target analytes or may employ other solid-phase media and extraction solvents, provided that the analyst demonstrates adequate performance (e.g., recovery of 70 - 130%, or at levels that meet project-specific recovery criteria) using spiked sample matrices and an appropriate determinative method of the type included as an 8000 series method in this manual. The use of organic-free reagent water alone is not considered sufficient for conducting such performance studies; performance must be supported by data from actual sample matrices.

1.3 This method may not be appropriate for aqueous samples with high levels of suspended solids greater than 1%. However, if the particulate matter is not considered to be part of the sample composition based on specific project objectives and intended data usage, samples may be allowed to settle before measuring the aliquot to be extracted. If significant particulate matter is present and the total sample is of concern, then the sample should be treated as a multi-phase sample per Chapter Two.

1.4 This method also provides procedures for concentrating extracts and for solvent exchange.

1.5 Solid-phase extraction is called liquid-solid extraction (LSE) in some methods associated with the Safe Drinking Water Act.

1.6 Prior to employing this method, analysts are advised to consult the base method for each type of procedure that may be employed in the overall analysis (e.g., Methods 3500, 3600, 5000, and 8000) for additional information on quality control procedures, development of QC acceptance criteria, calculations, and general guidance. Analysts also should consult the disclaimer statement at the front of the manual and the information in Chapter Two for guidance on the intended flexibility in the choice of methods, apparatus, materials, reagents, and supplies, and on the responsibilities of the analyst for demonstrating that the techniques employed are appropriate for the analytes of interest, in the matrix of interest, and at the levels of concern.

In addition, analysts and data users are advised that, except where explicitly specified in a regulation, the use of SW-846 methods is *not* mandatory in response to Federal testing requirements. The information contained in this method is provided by EPA as guidance to be used by the analyst and the regulated community in making judgments necessary to generate results that meet the data quality objectives for the intended application.

1.7 Use of this method is restricted to use by, or under supervision of, appropriately experienced and trained personnel. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 Sample preparation procedures vary by analyte group. For the extraction of some analyte groups, the pH of the sample is adjusted to a specified value prior to extraction (see Sec. 11.2). Other groups do not need a pH adjustment.

2.2 Following any necessary pH adjustment, a measured volume of sample is extracted by passing it through the solid-phase extraction medium (disks or cartridges), which is held in an extraction device designed for vacuum filtration of the sample.

2.3 Target analytes are eluted from the solid-phase media using an appropriate solvent (see Secs. 11.7 and 11.8.7) which is collected in a receiving vessel. The resulting solvent extract is dried using sodium sulfate and concentrated, as needed.

2.4 As necessary for the specific analysis, the concentrated extract may be exchanged into a solvent compatible extract with subsequent cleanup procedures (see the 3600 series of methods) or determinative procedures (see the 8000 series of methods) for the measurement of the target analytes.

3.0 DEFINITIONS

Refer to Chapter One and the manufacturer's instructions for definitions that may be relevant to this procedure.

4.0 INTERFERENCES

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be necessary. Refer to each method to be used for specific guidance on quality control procedures and refer to Chapter Four for general guidance on the cleaning of glassware. Also refer to Method 3500 for additional information regarding interferences and quality control procedures.

4.2 The decomposition of some analytes has been demonstrated under basic extraction conditions. Organochlorine pesticides may dechlorinate and phthalate esters may hydrolyze. The rates of these reactions increase with increasing pH and reaction times.

4.3 Bonded-phase silica (e.g., C_{18}) will hydrolyze on prolonged exposure to aqueous samples with pH levels of less than 2 or greater than 9. Hydrolysis will increase at the extremes of this pH range and with longer contact times. Hydrolysis may reduce extraction efficiency or cause baseline irregularities. Styrene divinylbenzene (SDB) extraction disks should be considered when hydrolysis is a problem.

4.4 Phthalates are ubiquitous laboratory contaminants. All-glass extraction apparatus should be used for this method because phthalates are used as release agents when molding rigid plastic (e.g., PVC) and as plasticizers for flexible tubing. A method blank should be analyzed, demonstrating that there is no phthalate contamination of the sodium sulfate or other reagents listed in this method.

4.5 Sample particulates may clog the solid-phase media and result in extremely slow sample extractions. Use of an appropriate filter aid will result in shorter extractions without loss of method performance if clogging is a problem. Even when a filter aid is employed, this method may not be appropriate for aqueous samples with high levels of suspended solids (>1%), as the extraction efficiency may not be sufficient, given the small volumes of solvents employed and the short contact time.

5.0 SAFETY

5.1 This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals listed in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses.

5.2 When handling samples that contain explosives, carefully follow the concentration instructions of this method. Otherwise, THE EXPLOSIVES MAY DETONATE!

6.0 EQUIPMENT AND SUPPLIES

The mention of trade names or commercial products in this manual is for illustrative purposes only, and does not constitute an EPA endorsement or exclusive recommendation for use. The products and instrument settings cited in SW-846 methods represent those products and settings used during method development or subsequently evaluated by the Agency. Glassware, reagents, supplies, equipment, and settings other than those listed in this manual may be employed provided that method performance appropriate for the intended application has been demonstrated and documented. The apparatus and materials described in this method are based on data provided to EPA for the extraction of eight groups of analytes using disk-type materials and for the extraction of one group of analytes using cartridge-type materials. Other solid-phase extraction media configurations may be employed, provided that method performance appropriate for the intended application has been demonstrated and documented. The procedures described in Sec. 11.0 need to be modified for the use of another SPE configuration. Consult the manufacturer's instructions regarding such modifications.

This section does not list common laboratory glassware (e.g., beakers and flasks).

6.1 Solid-phase disk extraction system -- Empore™ manifold that holds three 90-mm filter standard apparatus or six 47-mm standard filter apparatus, or equivalent. Other manual, automatic, or robotic sample preparation systems designed for solid-phase media may be utilized for this method if adequate performance is achieved and all project quality control requirements are satisfied.

6.1.1 Manifold station -- Fisher Scientific 14-378-1B [3-place], 14-378-1A [6-place], or equivalent.

6.1.2 Standard filter apparatus -- Fisher Scientific 14-378-2A [47-mm], 14-378-2B [90-mm], or equivalent, consisting of a sample reservoir, clamp, fritted disk and filtration head equipped with drip tip.

6.1.3 Collection tube -- 60-mL. The collection tube should have an appropriate ID and length so that the drip tip of the standard filter apparatus can be positioned well into the neck of the tube to prevent splattering.

6.1.4 Filter flask -- 2-L equipped with a ground-glass receiver joint (optional). May be used to carry out individual disk extractions with the standard filter apparatus and collection vial in an all-glass system.

6.2 Solid-phase cartridge extraction system -- Visiprep solid-phase extraction manifold (Supelco) or equivalent system suitable for use with the extraction cartridges (see Sec. 6.4).

Consult the manufacturer's recommendations for the associated glassware and hardware necessary to perform sample extractions.

6.3 Solid-phase extraction disks -- Empore™, 47-mm, 90-mm, or equivalent. Disks are available in 47-mm and 90-mm diameters, composed of a variety of solid-phase materials. Other solid phases may be employed, provided that adequate performance is demonstrated for the analytes of interest. Guidance for selecting the specific disk is provided in Table 1.

6.3.1 C_{18} disks -- Empore™ disks, 47-mm diameter (3M product number 98-0503-0015-5), 90-mm diameter (3M product number 98-0503-0019-7), or equivalent.

6.3.2 C_{18} fast flow disks -- Empore™ disks, 47-mm diameter (3M product number 98-0503-0138-5), 90-mm diameter (3M product number 98-0503-0136-9), or equivalent. These disks may be a better choice for samples that are difficult to filter even with the use of a filter aid.

6.3.3 Styrene divinylbenzene (SDB-XC) disks -- Empore™ disks, 47-mm diameter (3M product number 98-0503-0067-6), 90-mm diameter (3M product number 98-0503-0068-4), or equivalent.

6.3.4 Styrene divinylbenzene reversed-phase sulfonated (SDB-RPS) disks -- Empore™ disks, 47-mm diameter (3M product number 98-0503-0110-4), 90-mm diameter (3M product number 98-0503-0111-2), or equivalent.

6.4 Solid-phase extraction cartridges -- Porapak® R SPE device, Waters Corporation, or equivalent. Other solid phases may be employed, provided that adequate performance is demonstrated for the analytes of interest.

6.5 Filtration aid (optional)

6.5.1 Filter Aid 400 -- (Fisher Scientific 14-378-3, or equivalent).

6.5.2 In-situ glass micro-fiber prefilter -- (Whatman GMF 150, 1-µm pore size, or equivalent).

6.6 Drying column -- 22-mm ID glass chromatographic column equipped with a PTFE stopcock (Kontes K-420530-0242, or equivalent).

NOTE: Fritted glass discs used to retain sodium sulfate in some columns may be difficult to decontaminate after contact with highly contaminated or viscous extracts. Columns suitable for this method use a small pad of glass wool to retain the drying agent.

6.7 Kuderna-Danish (K-D) apparatus

6.7.1 Concentrator tube -- 10-mL, graduated. A ground-glass stopper is used to prevent evaporation of extracts during short-term storage.

6.7.2 Evaporation flask -- 500-mL, or other size appropriate for the volumes of solvents to be concentrated. Attach to concentrator tube using springs or clamps.

6.7.3 Three-ball macro-Snyder column.

6.7.4 Two-ball micro-Snyder column (optional).

6.7.5 Springs -- ½-inch.

6.8 Solvent vapor recovery system -- Kontes 545000-1006 or K-547300-0000, Ace Glass 6614-30, or equivalent.

NOTE: This glassware is recommended for the purpose of solvent recovery during the concentration procedures (see Secs. 11.9 and 11.10) using the Kuderna-Danish evaporative concentrators. Incorporation of this apparatus may be required by Federal, State or local municipality regulations that govern air emissions of volatile organics. EPA recommends the incorporation of this type of reclamation system as a method to implement an emissions reduction program. Solvent recovery is a means to conform with waste minimization and pollution prevention initiatives.

6.9 Boiling chips -- Solvent extracted, approximately 10/40 mesh (silicon carbide, or equivalent).

6.10 Water bath -- Heated, equipped with concentric ring cover, capable of temperature control to within ± 5 EC. The bath should be used in a hood.

6.11 Nitrogen evaporation apparatus (optional) -- N-Evap, 12- or 24-position (Organomation Model 112, or equivalent).

6.12 Vials, glass -- Sizes as appropriate, e.g., 2-mL or 10-mL, equipped with polytetrafluoroethylene (PTFE)-lined screw caps or crimp tops for storage of extracts.

6.13 pH indicator paper -- Wide pH range.

6.14 Vacuum system -- Capable of maintaining a vacuum of approximately 66 cm (26 inches) of mercury.

6.15 Graduated cylinders -- Sizes as appropriate.

6.16 Pipets -- disposable.

6.17 Disposable cartridge filters, 0.45 micron (Millex SR or equivalent).

7.0 REAGENTS AND STANDARDS

7.1 Reagent grade chemicals must be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without decreasing the accuracy of the determination. Reagents should be stored in glass to prevent the leaching of contaminants from plastic containers.

7.2 Organic-free reagent water -- All references to water or reagent water in this method refer to organic-free reagent water, as defined in Chapter One.

7.3 Sodium sulfate (granular, anhydrous), Na_2SO_4 -- Purify by heating at 400 EC for 4 hrs in a shallow tray, or by precleaning the sodium sulfate with methylene chloride.

7.4 Solutions for adjusting the pH of samples before extraction

7.4.1 Sulfuric acid solution (1:1 v/v), H_2SO_4 -- Slowly add 50 mL of concentrated H_2SO_4 (sp. gr. 1.84) to 50 mL of organic-free reagent water.

7.4.2 Sodium hydroxide solution (10N), NaOH -- Dissolve 40 g of NaOH in organic-free reagent water and dilute to 100 mL.

7.5 Extraction, washing, and exchange solvents

This method has been validated using a combination of the solvents recommended in Sec. 11.0. Other solvents may have applicability in solid-phase extraction, provided that acceptable performance that meets the project requirements can be demonstrated for the intended target analytes.

The choice of extraction solvent will depend on the analytes of interest and no single solvent is universally applicable to all analyte groups. Whatever solvent is employed, *including* those specifically listed in this method, the analyst *must* demonstrate adequate performance for the analytes of interest, at the levels of interest. At a minimum, such a demonstration will encompass the initial demonstration of proficiency described in Method 3500, using a clean reference matrix. Method 8000 describes procedures that may be used to develop performance criteria for such demonstrations as well as for matrix spike and laboratory control sample results.

At a minimum, all solvents must be pesticide quality or equivalent. Solvents may be degassed prior to use.

7.5.1 Methylene chloride, CH_2Cl_2.

7.5.2 Hexane, C_6H_{14}.

7.5.3 Ethyl acetate, $CH_3COOCH_2CH_3$.

7.5.4 Acetonitrile, CH_3CN.

7.5.5 Methanol, CH_3OH.

7.5.6 Acetone, $(CH_3)_2CO$.

7.5.7 Methyl-*tert*-butyl ether (MTBE), $C_5H_{12}O$.

7.5.8 Isopropanol, $(CH_3)_2CHOH$.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

See Secs. 11.1 and 11.2 of this method. Also see the introductory material to Chapter Four, "Organic Analytes," Method 3500, and the specific determinative methods to be employed.

9.0 QUALITY CONTROL

9.1 Refer to Chapter One for additional guidance on quality assurance (QA) and quality control (QC) protocols. When inconsistencies exist between QC guidelines, method-specific QC criteria take precedence over both technique-specific criteria and those criteria given in Chapter One, and technique-specific QC criteria take precedence over the criteria in Chapter One. Any effort involving the collection of analytical data should include development of a structured and systematic planning document, such as a Quality Assurance Project Plan (QAPP) or a Sampling and Analysis Plan (SAP), which translates project objectives and specifications into directions for those that will implement the project and assess the results. Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated. All data sheets and quality control data should be maintained for reference or inspection.

9.2 Initial demonstration of proficiency

Each laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes by generating data of acceptable accuracy and precision for target analytes in a clean matrix. The laboratory must also repeat the demonstration of proficiency whenever new staff members are trained or significant changes in instrumentation are made. See Method 8000 for information on how to accomplish a demonstration of proficiency.

9.3 Initially, before processing any samples, the analyst should demonstrate that all parts of the equipment in contact with the sample and reagents are interference-free. This is accomplished through the analysis of a method blank. As a continuing check, each time samples are extracted, cleaned up, and analyzed, and when there is a change in reagents, a method blank should be prepared and analyzed for the compounds of interest as a safeguard against chronic laboratory contamination.

9.4 Any method blanks, matrix spike samples, or replicate samples should be subjected to the same analytical procedures (Sec. 11.0) as those used on actual samples.

9.5 Standard quality assurance practices should be used with this method as included in appropriate systematic planning documents and laboratory SOPs. All instrument operating conditions should be recorded.

9.6 Also refer to Method 3500 for extraction and sample preparation quality control procedures and the determinative methods to be used for determinative QC procedures.

9.7 When listed in the appropriate determinative method, surrogate standards should be added to all samples prior to extraction. See Methods 3500 and 8000, and the appropriate determinative methods for more information.

9.8 As noted earlier, use of any extraction technique, including solid-phase extraction, should be supported by data that demonstrate the performance of the specific solvent system and operating conditions for the analytes of interest, at the levels of interest, in the sample matrix.

10.0 CALIBRATION AND STANDARDIZATION

There are no calibration or standardization steps directly associated with this extraction procedure.

11.0 PROCEDURE

The procedures for solid-phase extraction are very similar for most organic analytes. The procedures for sample preparation (Sec. 11.1), pH adjustment (Sec. 11.2), setting up the extraction apparatus (Sec. 11.3), and information regarding extract concentration generally apply to all target analytes. The procedures for disk washing (Sec. 11.4), disk conditioning (Sec. 11.5), sample extraction (Sec. 11.6), and sample elution (Sec. 11.7) vary among the groups of analytes. Sec. 11.8 provides procedural information regarding use of the SPE cartridge technique for nitroaromatics, nitramines, and explosives. Sec. 11.9 provides procedural information regarding the K-D concentration technique and, if further concentration is necessary, Sec. 11.10 provides procedural information regarding both the micro-Snyder column technique and the nitrogen evaporation technique.

11.1 Sample preparation

Most of the specific procedures described in this method were developed for a nominal sample size of 1 L, because this sample size is usually employed for other extraction methods such as separatory funnel or continuous liquid-liquid extraction. This method also may be employed with a smaller sample size when overall analytical sensitivity is not a concern or when high levels of the target analytes are anticipated. However, such samples are best collected in an appropriately-sized container. For optimized analytical results, the entire sample must be used.

The extraction of aqueous samples presents several challenges that must be considered during sample preparation. First, if the specific project requirements indicate that the analytes of interest are associated with the particulate matter in the sample, the sample preparation procedures must ensure that any particulates in the original sample are included in the sample aliquot that is extracted. However, the efficiency of the extraction media may be affected when samples containing greater than 1% solids are fully extracted. For some applications, it may be desirable to quantitate only the soluble constituents based on the stated project objectives and the intended uses of the data. In these situations, samples containing particulates may be allowed to settle before measuring the aliquot to be extracted. Conversely, if significant particulate matter is present and the total constituent concentration is necessary, the sample phases may be spilt, with the aqueous phase extracted using this method and the solid phase extracted using an appropriate extraction technique based on the target analytes. The sample extracts then can be either analyzed separately or combined for a single analysis. Secondly, the majority of the organic analytes are hydrophobic and may preferentially adhere to the surfaces of the sample container. For this reason, most extraction methods have traditionally specified that, once the sample is transferred to the extraction apparatus, the sample container should be rinsed with solvent which is added to the apparatus. As a result, it is generally <u>not</u> appropriate to extract only part of the sample from a sample container, e.g., 250 mL from a 1-L sample bottle.

The appropriate sample volume may vary with the intended use of the results and, in general, is the volume necessary to provide the analytical sensitivity necessary to meet the objectives of the project (see Chapter Two). Under ideal conditions, the sample should be collected by completely filling the container. The sample should generally be collected without additional volume and with little or no headspace. Thus, a 1-L sample is collected in a 1-L container, a 250-mL sample is collected in a 250-mL container, not a 1-L container, etc.

<u>CAUTION</u>: The presence of light will cause photodegradation of several polyaromatic hydrocarbons. If this class of compounds includes target analytes, the samples

should be extracted away from light sources, and preferably in darker environments.

Any surrogates and matrix spiking compounds (if applicable) are added to the sample in the original container. The container is then recapped and shaken to mix the spiked analytes into the sample. For some groups of analytes, the pH of the sample needs to be adjusted to a designated value (see Table 1). When pH adjustment is necessary, it should be performed after the surrogates and matrix spiking compounds (if applicable) have been added and mixed with the sample. Otherwise, the recoveries of these compounds will have little relevance to those of the target analytes in the sample.

If this approach is not possible, then a sample aliquot may be transferred to a graduated cylinder and spiked. However, in such instances, the analyst must take great care to mix the sample well, by shaking, to ensure a homogeneous distribution of the particulate matter and must record the fact that the container was not rinsed.

NOTE: This method may not be appropriate for aqueous samples with greater than 1% solids, as such samples can be difficult to filter and the extraction efficiency may be reduced as a result of the small volumes of solvents employed and the short contact time. If the particulate load significantly slows or prevents filtration, it may be more appropriate to employ an alternative extraction procedure.

11.1.1 Mark the level of the sample on the outside of the sample container for later determination of the sample volume used. Shake the container for several minutes, with the cap tightly sealed, to ensure that any particulate matter is evenly distributed throughout the sample.

11.1.2 Prepare a method blank from a 1-L volume of organic-free reagent water, or a volume of reagent water similar to that being used for the samples (e.g., a 250-mL blank should be used when the sample size is 250 mL, etc.). The blank may be prepared in a graduated cylinder, beaker, or other suitable container. Chapter One provides guidelines regarding the frequency of method blank preparation.

11.1.3 Add any surrogate standards listed in the determinative method to the samples in their original containers and to the blank.

11.1.4 Shake the samples to mix the surrogates and allow the sample to stand for at least several minutes. This will permit the surrogates to dissolve in the sample and will also allow the particulate matter to settle after spiking, which will speed the filtration process.

11.1.5 Prepare matrix spikes by adding listed matrix spike standards to representative sample replicates in their original containers. Chapter One or the determinative method provide guidelines regarding the frequency of matrix spike preparation. For disk extractions, add 5.0 mL of methanol after spiking the samples. Mix the matrix spike samples as described in Sec.11.1.4 and allow to stand.

11.1.6 If cleanup procedures are to be employed that result in the loss of extract, adjust the amount of surrogate and spiking cocktail(s) accordingly. In the case of Method 3640, Gel Permeation Cleanup, it may be necessary to double the amount of standards to compensate for the loss of one half of the extract concentrate when loading the GPC column.

11.2 pH adjustment

Check the pH of the sample with wide-range pH paper and, if necessary, adjust the pH to the range listed below. If pH adjustment is needed, this step should be performed in the original sample container to ensure that analytes are not lost in precipitates or flocculated material. Any adjustment of the sample pH should take place after the surrogates and matrix spiking compounds are added, so that they are affected by the pH in the same manner as the target analytes.

CAUTION: Depending on the target analytes, dechlorination may be necessary at the time of sample collection. Any pH adjustment that is needed for extraction should always be performed after the dechlorination step.

NOTE: The efficiency of solid-phase extraction of acid herbicide compounds is greatly affected by pH. If acid herbicides are to be extracted from TCLP leachates or other samples, adjust the pH to 1.0 before extraction.

Analyte Group	Extraction pH
Phthalate esters	5 - 7
Organochlorine pesticides	5 - 9
Polychlorinated biphenyls (PCBs)	5 - 9
Organophosphorus pesticides	as received
Nitroaromatics and nitramines	as received
Explosives	as received
TCLP leachates containing organochlorine pesticides	as produced by TCLP
TCLP leachates containing semivolatiles	as produced by TCLP
TCLP leachates containing phenoxyacid herbicides	1.0

11.3 Setting up the extraction apparatus

11.3.1 Assemble a manifold for multiple disk extractions using 47-mm or 90-mm extraction disks. Use a filter flask equipped with the standard filter apparatus (Figure 1) for single extractions, using 47-mm or 90-mm extraction disks. The solid-phase disks that are generally appropriate for each group of analytes are listed below, and in Table 1.

Analyte Group	Disk Medium
Phthalate esters	C_{18}
Organochlorine pesticides	C_{18}
Polychlorinated biphenyls (PCBs)	C_{18}
Organophosphorus pesticides	SDB-RPS
Nitroaromatics and nitramines	SDB-RPS
Explosives	SDB-RPS
TCLP leachates containing organochlorine pesticides	SDB-XC
TCLP leachates containing semivolatiles	SDB-XC

Analyte Group	Disk Medium
TCLP leachates containing phenoxyacid herbicides	SDB-XC

Samples also may be extracted using an SPE cartridge for nitroaromatics, nitramines, and explosives. Assemble the cartridge apparatus according to the manufacturer's instructions, using Porapak R, or equivalent, SPE cartridges, and proceed to Sec. 11.8.

11.3.2 If samples contain significant quantities of particulates, the use of a filter aid or prefilter is advisable for disk extractions. Empore™ Filter Aid 400, Whatman GMF 150, or equivalent prefilters are recommended.

11.3.2.1 Pour about 40 g of Filter Aid 400 onto the surface of the disk after assembling the standard filter apparatus.

11.3.2.2 Alternatively, place the Whatman GMF 150 on top of the extraction disk prior to clamping the glass reservoir into the standard filter apparatus.

11.3.2.3 Do not add the filter aid if using the cartridge extraction procedure for nitroaromatics, nitramines, or explosives (Sec. 11.8).

11.4 Washing the extraction apparatus

Prior to use, the extraction disks must undergo two separate washing steps, usually with different solvents. The steps involved in washing the extraction apparatus before use depend on the analytes of interest and the sample matrix.

11.4.1 First washing step

The following table illustrates the solvents recommended for the first washing step.

Analyte Group	1st solvent wash volume
Phthalate esters	20 mL methylene chloride
Organochlorine pesticides	20 mL methylene chloride
Polychlorinated biphenyls (PCBs)	20 mL methylene chloride
Organophosphorus pesticides	5 mL acetone
Nitroaromatics and nitramines	5 mL acetonitrile
Explosives	5 mL acetone
TCLP leachates containing organochlorine pesticides	5 mL acetone
TCLP leachates containing semivolatiles	5 mL acetone
TCLP leachates containing phenoxyacid herbicides	5 mL acetonitrile

Wash the extraction apparatus and disk with the volume of the solvent listed above by rinsing the solvent down the sides of the glass reservoir. Pull a small amount of solvent through the disk with a vacuum. Turn off the vacuum and allow the disk to soak for about one minute. Pull the remaining solvent through the disk and allow the disk to dry.

11.4.1.1 When using a filtration aid, adjust the volume of all wash solvents so the entire filtration bed is submerged.

11.4.1.2 In subsequent conditioning steps, volumes should be adjusted so that a level of solvent is always maintained above the entire filter bed.

11.4.2 Second washing step

The following table illustrates the solvents recommended for the second washing step.

Analyte Group	2nd solvent wash volume
Phthalate esters	10 mL acetone
Organochlorine pesticides	10 mL acetone
Polychlorinated biphenyls (PCBs)	not needed
Organophosphorus pesticides	5 mL methanol
Nitroaromatics and nitramines	15 mL acetonitrile
Explosives	15 mL isopropanol
TCLP leachates containing organochlorine pesticides	5 mL ethyl acetate
TCLP leachates containing semivolatiles	5 mL ethyl acetate
TCLP leachates containing phenoxyacid herbicides	not needed

11.4.3 Third washing step

The third washing step only applies to explosives.

Analyte Group	3rd solvent wash volume
Explosives	15 mL methanol

11.5 Disk conditioning

The extraction disks are composed of hydrophobic materials which will not allow water to pass unless the disks are pre-wetted with a water-miscible solvent before use for sample extraction. This step is referred to as conditioning, and the solvent used is dependent on the analytes of interest. The following table illustrates the solvents recommended for specific groups of analytes.

CAUTION: Beginning with the conditioning step, it is CRITICAL that the disk NOT go dry until after the extraction steps are completed. Should a disk accidentally go dry during the conditioning steps, the conditioning steps for that disk MUST be repeated prior to adding the sample.

Analyte Group	Conditioning steps
Phthalate esters	20 mL methanol, soak 1 min, 20 mL reagent water

Analyte Group	Conditioning steps
Organochlorine pesticides	20 mL methanol, soak 1 min, 20 mL reagent water
Polychlorinated biphenyls (PCBs)	20 mL methanol, soak 1 min, 20 mL reagent water
Organophosphorus pesticides	5 mL methanol, soak 1 min, 20 mL reagent water
Nitroaromatics and nitramines	15 mL acetonitrile, soak 3 min 30 mL reagent water
Explosives	20 mL acetonitrile, soak 3 min 20 mL acetonitrile 50 mL reagent water 50 mL reagent water
TCLP leachates containing organochlorine pesticides	5 mL methanol soak 1 min, 15 mL reagent water
TCLP leachates containing semivolatiles	5 mL methanol soak 1 min, 15 mL reagent water
TCLP leachates containing phenoxyacid herbicides	5 mL methanol soak 1 min, 15 mL reagent water

11.5.1 Add the conditioning solvent to the extraction apparatus. Apply a vacuum until a few drops of solvent pass through the disk, ensuring that the disk is soaked with solvent. Turn off the vacuum and allow the disk to soak in the solvent for the time listed above.

11.5.2 When using a filtration aid, adjust the volume of conditioning solvents so that the entire filtration bed remains submerged until the extraction is completed.

11.5.3 Once the soaking time is over, apply the vacuum again, drawing all but a thin layer of solvent through the disk. Stop the vacuum just before the disk goes dry.

11.5.4 Add the volume of organic-free reagent water listed above and apply vacuum to draw the water through the disk. Stop the vacuum just before the disk goes dry, leaving 2-3 mm of water above the surface of the disk.

11.5.5 The disks used for explosives need two rinses with acetonitrile and two rinses with reagent water.

11.6 Sample extraction using SPE disks

11.6.1 After performing the washing and conditioning steps, pour the sample into the reservoir and, under full vacuum, filter it as quickly as the vacuum will allow (at least 10 min). Transfer as much of the measured volume of water as possible.

NOTE: With heavily particle-laden samples, allow the sediment in the sample to settle and decant as much liquid as is practical into the reservoir. Reduce the vacuum level to minimize pulling the particles into the disk structure. After most of the

aqueous portion of the sample has passed through the disk, swirl the portion of the sample containing sediment and add it to the reservoir. Use additional portions of organic-free reagent water to transfer any remaining particulates to the reservoir. Particulates must be transferred to the reservoir before all of the aqueous sample has passed through the disk. Alternatively, for some applications it may be desirable to quantitate only the soluble constituents based on the stated project objectives and the intended use of the data. In those situations, samples containing particulates may be allowed to settle with the intention of excluding the particulate matter from extraction.

11.6.2 After the sample has passed through the solid-phase media, dry the disk by maintaining vacuum for about 3 min. Method blanks and matrix spike aliquots (see Sec. 11.1) are handled in the same manner as the samples.

NOTE: Maintain the vacuum for 20 min when drying the disks used for the explosives, however, for other target analytes that may be sensitive to oxidation the drying time should be kept to a minimum.

11.7 Elution of the analytes from the disk

The choice of elution solvent is critical to the success of solid-phase extraction. The recommended elution solvents for each group of analytes are listed below.

Analyte Group	Sample elution steps
Phthalate esters	5 mL acetone, soak 15-20 sec. Rinse bottle with 15 mL acetonitrile and add to disk.
Organochlorine pesticides	5 mL acetone, soak 15-20 sec. Rinse bottle with 15 mL methylene chloride and add to disk.
Polychlorinated biphenyls (PCBs)	5 mL acetone, soak 15-20 sec. Rinse bottle with 20 mL acetonitrile and add to disk.
Organophosphorus pesticides	0.6 mL acetone, soak 1 min. Rinse bottle with 5 mL MTBE and add to disk. Repeat bottle rinse twice more.
Nitroaromatics and nitramines	5 mL acetonitrile, soak 3 min.
Explosives	4 mL acetonitrile, soak 3 min.
TCLP leachates containing organochlorine pesticides	Rinse bottle with 4 mL acetone and add to disk. Rinse glassware with 2 mL acetone and add to disk. Soak 1 min. Rinse bottle twice with 5 mL ethyl acetate and add to disk.
TCLP leachates containing semivolatiles	Rinse bottle with 4 mL acetone and add to disk. Rinse glassware with 2 mL acetone and add to disk. Soak 1 min. Rinse bottle twice with 5 mL ethyl acetate and add to disk.
TCLP leachates containing phenoxyacid herbicides	Rinse bottle with 5 mL acetonitrile and add to disk. Soak 1 min. Rinse bottle twice more with 5 mL acetonitrile and add to disk.

11.7.1 Remove the entire standard filter assembly (do not disassemble) from the manifold and insert a collection tube. The collection tube should have sufficient capacity

to hold all of the elution solvents. The drip tip of the filtration apparatus should be seated sufficiently below the neck of the collection tube to prevent analyte loss due to splattering when vacuum is applied. When using a filter flask for single extractions, empty the water from the flask before inserting the collection tube.

11.7.2 An initial elution with a water-miscible solvent, i.e., acetone or acetonitrile, improves the recovery of analytes trapped in water-filled pores of the sorbent. Use of a water-miscible solvent is particularly critical when methylene chloride is used as the second elution solvent. With the collection tube in place, add the volume of elution solvent listed above to the extraction apparatus. Allow the solvent to spread out evenly across the disk (or inert filter) then quickly turn the vacuum on and off to pull the first drops of solvent through the disk. Allow the disk to soak for the periods indicated above before proceeding to Sec. 11.7.3.

11.7.3 Rinse the sample bottle and/or glassware that held the sample with the second solvent listed above and transfer the solvent rinse to the extraction apparatus. As needed, use a disposable pipette to rinse the sides of the extraction apparatus with solvent from the bottle.

NOTE: These bottle rinsing steps may be omitted if the particulate matter in the bottom of the sample bottle is purposely being excluded from extraction due to the project requirements. However, the recommended solvent should still be added directly to the extraction apparatus.

11.7.4 Draw about half of the solvent through the disk and then release the vacuum. Allow the remaining elution solvent to soak the disk and particulates for about one minute before drawing the remaining solvent through the disk under vacuum. When using a filtration aid, adjust the volume of elution solvent so that the entire filtration bed is initially submerged.

11.7.5 Repeat the bottle rinsing step as listed in the table above, continuing to apply vacuum and collecting the solvent in the tube.

11.7.6 If the extract is turbid, filter through a Millex-SR filter unit, or equivalent

WARNING: Do NOT concentrate explosives any further. THE EXPLOSIVES MAY DETONATE!

11.8 Cartridge technique for nitroaromatics, nitramines, and explosives

Aqueous samples to be analyzed for nitroaromatics, nitramines, and explosives may also be extracted using the SPE cartridge technique described below. The same sample preparation considerations discussed in Sec. 11.1 also apply to this procedure.

Analyte Group	Washing steps
Nitroaromatics and nitramines	10 mL acetonitrile 30 mL reagent water
Explosives	30 mL acetonitrile 50 mL reagent water

11.8.1 After assembling the SPE cartridge in the extraction apparatus (see Sec. 11.3.1), wash the cartridge with the volume of acetonitrile listed above, using gravity flow. Do not allow the cartridge to go dry.

11.8.2 When only a thin layer of solvent remains above the sorbent bed in the cartridge, add the reagent water to the cartridge and allow it to flow through the sorbent bed under gravity flow. Stop the flow just before the cartridge goes dry.

11.8.3 Attach a connector to the top of the cartridge. The other end of the connector should be fitted with flexible PTFE tubing long enough to reach into the sample bottle or other container (e.g., a beaker) holding the sample.

11.8.4 Turn on the vacuum, and draw the sample through the cartridge at a rate of about 10 mL/min, until all of the sample has passed through the cartridge. As particulate matter plugs the cartridge and slows the flow, increase the vacuum to maintain a reasonable flow rate.

11.8.5 Follow the individual procedures below for nitroaromatics and nitramines or explosives.

11.8.5.1 Nitroaromatics and nitramines

Once all of the sample has been pulled through the cartridge, shut off the vacuum and add 5 mL of reagent water to the cartridge. Allow the reagent water to pass through the cartridge under gravity flow, if practical, or apply a vacuum to complete the process. Shut off the flow once the water has been drawn through the cartridge.

11.8.5.2 Explosives

Once all the sample has been drawn through a cartridge, draw air through the cartridge for 15 min in order to remove any excess water. Turn the vacuum off. Remove any drops of water that may be clinging to the cartridge tip.

11.8.6 Method blanks and matrix spike aliquots (see Sec. 11.1) are handled in the same manner as the samples.

11.8.7 Eluting the nitroaromatics and nitramines from the cartridge

Once the reagent water has passed through the column, place a collection tube under the cartridge. Add 5 mL of acetonitrile to the top of the cartridge and allow it to pass through the cartridge under gravity flow, collecting the solvent in the collection tube. Measure the actual volume (to the nearest 0.1 mL) of the solvent extract. If concentration of the extract is necessary, proceed to Sec. 11.9. Otherwise, store extracts in a freezer until analysis.

11.8.8 Eluting the explosives from the cartridge

Once the reagent water has passed through the column, place a collection tube under the cartridge. Add 4 mL (not 5 mL) of acetonitrile to the top of the cartridge and allow it to pass through the cartridge under gravity flow, collecting the solvent in the collection tube. Measure the actual volume (to the nearest 0.1 mL) of the solvent extract.

WARNING: Do NOT concentrate explosives any further. THE EXPLOSIVES MAY DETONATE!

Store extracts in a freezer until analysis.

11.9 K-D concentration technique

Where necessary to meet the sensitivity requirements of the particular application, sample extracts may be concentrated to the final volume necessary for the determinative method and specific application using the K-D technique or nitrogen evaporation.

WARNING: Do NOT concentrate explosives any further. THE EXPLOSIVES MAY DETONATE!

11.9.1 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to an appropriately-sized evaporation flask.

11.9.2 Dry the combined extracts in the collection tube (see Secs. 11.7.1 and 11.8.7) by passing them through a drying column containing about 10 g of anhydrous sodium sulfate. Collect the dried extract in the K-D concentrator. Use acidified sodium sulfate (see Method 8151) if acidic analytes are to be measured.

11.9.3 Rinse the collection tube and drying column into the K-D flask with an additional 20-mL portion of solvent in order to achieve a quantitative transfer.

11.9.4 Add one or two clean boiling chips to the flask and attach a three-ball Snyder column. Attach the solvent vapor recovery glassware (condenser and collection device, see Sec. 6.8) to the Snyder column of the K-D apparatus, following the manufacturer's instructions. Pre-wet the Snyder column by adding about 1 mL of methylene chloride (or other suitable solvent) to the top of the column. Place the K-D apparatus on a hot water bath (15 - 20 EC above the boiling point of the solvent) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as necessary to complete the concentration in 10 - 20 min. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 min.

11.9.4.1 If a solvent exchange is needed (as indicated in Table 1), momentarily remove the Snyder column, add 50 mL of the exchange solvent and a new boiling chip.

11.9.4.2 Reattach the Snyder column. Concentrate the extract, raising the temperature of the water bath, if necessary, to maintain a proper distillation rate.

11.9.5 Remove the Snyder column. Rinse the K-D flask and the lower joints of the Snyder column into the concentrator tube with 1 - 2 mL of solvent. The extract may be further concentrated by using one of the techniques outlined in Sec. 11.10, or adjusted to a final volume of 5.0 - 10.0 mL using an appropriate solvent (see Table 1).

11.10 If further concentration is necessary, use either the micro-Snyder column technique (see Sec. 11.10.1) or the nitrogen evaporation technique (see Sec. 11.10.2).

WARNING: Do NOT concentrate explosives any further. THE EXPLOSIVES MAY DETONATE.

11.10.1 Micro-Snyder column technique

11.10.1.1 Add a fresh clean boiling chip to the concentrator tube and attach a two-ball micro-Snyder column directly to the concentrator tube. Attach the solvent vapor recovery glassware (condenser and collection device) to the micro-Snyder column of the K-D apparatus, following the manufacturer's instructions. Pre-wet the Snyder column by adding 0.5 mL of methylene chloride or the exchange solvent to the top of the column. Place the micro-concentration apparatus in a hot water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as necessary, to complete the concentration in 5 - 10 min. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood.

11.10.1.2 When the apparent volume of liquid reaches 0.5 mL, remove the apparatus from the water bath and allow it to drain and cool for at least 10 min. Remove the Snyder column and rinse its lower joints into the concentrator tube with 0.2 mL of solvent. Adjust the final extract volume to 1.0 - 2.0 mL.

11.10.2 Nitrogen evaporation technique

11.10.2.1 Place the concentrator tube in a warm bath (30 EC) and evaporate the solvent volume to 0.5 mL using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon).

CAUTION: New plastic tubing must not be used between the carbon trap and the sample, since it may introduce phthalate interferences.

11.10.2.2 Rinse down the internal wall of the concentrator tube several times with solvent during the concentration. During evaporation, position the concentrator tube to avoid condensing water into the extract. Under normal procedures, the extract must not be allowed to become dry.

CAUTION: When the volume of solvent is reduced below 1 mL, some semivolatile analytes such as cresols may be lost.

11.11 The extract may now be subjected to cleanup procedures or analyzed for the target analytes using the appropriate determinative technique(s). If further handling of the extract will not be performed immediately, stopper the concentrator tube and store in a refrigerator. If the extract will be stored longer than 2 days, it should be transferred to a vial equipped with a PTFE-lined screw-cap, labeled appropriately, and stored in a refrigerator.

12.0 DATA ANALYSIS AND CALCULATIONS

There are no calculations explicitly associated with this extraction procedure. See the appropriate determinative method for calculation of final sample results.

13.0 METHOD PERFORMANCE

Refer to the appropriate determinative methods (e.g., those listed in Sec. 1.1) for any performance data examples and guidance related to solid-phase extraction. Performance data and related information are provided in SW-846 methods only as examples and guidance. The data do not represent required performance criteria for users of the methods. Instead, performance criteria should be developed on a project-specific basis, and the laboratory should establish in-house QC performance criteria for the application of this method. These performance data are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions consult *Less is Better: Laboratory Chemical Management for Waste Reduction* available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St., N.W. Washington, D.C. 20036, http://www.acs.org.

15.0 WASTE MANAGEMENT

The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* available from the American Chemical Society at the address listed in Sec. 14.2.

16.0 REFERENCES

1. V. Lopez-Avila, W. Beckert, et. al., "Single Laboratory Evaluation of Method 8060 - Phthalate Esters," EPA/600/4-89/039.

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3. C. Markell, "3M Data Submission to EPA," letter to B. Lesnik, June 27, 1995.

4. T. F. Jenkins, P.G. Thorne, K. F. Myers, E. F. McCormick, D. E. Parker, and B. L. Escalon, "Evaluation of Clean Solid Phases for Extraction of Nitroaromatics and Nitramines from

Water," USACE Cold Regions Research and Engineering Laboratory, Special Report 95-22, 1995.

5. M. E. Walsh, and T. Ranney, "Determination of Nitroaromatic, Nitramine, and Nitrate Ester Explosives in Water Using Solid Phase Extraction and GC-ECD," *Proceedings of the 13th Annual Waste Testing and Quality Assurance Symposium*, July 6-9, 1997, Arlington, VA.

6. M. E. Walsh and T. Ranney (1998), "Determination of Nitroaromatic, Nitramine, and nitrate ester explosives in water using SPE and GC-ECD: Comparison with HPLC," CRREL Report 98-2, U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, NH, 1998.

7. M. E. Walsh and T. Ranney, "Determination of Nitroaromatic, Nitramine, and Nitrate Ester Explosives in Water using Solid-phase Extraction and Gas Chromatography-electron Capture Detection: Comparison with High-performance Liquid Chromatography," *Journal of Chromatographic Science*, 36, pp. 406-416, 1998.

17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

The following pages contain the table and figure referenced by this method.

TABLE 1
RECOMMENDED DISK EXTRACTION CONDITIONS FOR VARIOUS DETERMINATIVE METHODS

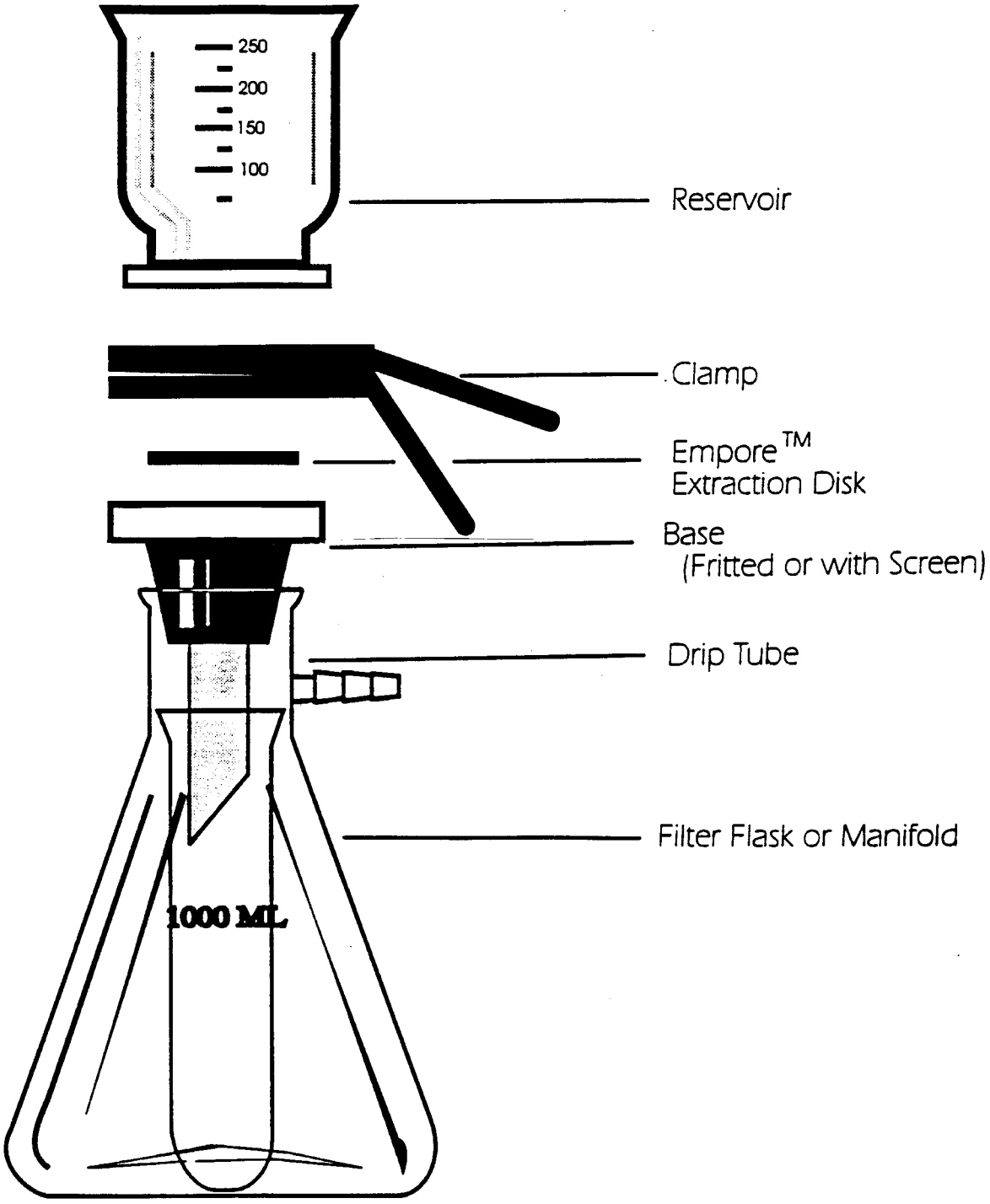
Determinative Method	Extraction pH	Disk Medium[a]	Elution Solvent	Exchange Solvent	Final Extract Volume for Analysis (mL)[b]
8061 (phthalate esters)	5-7	C_{18}	acetonitrile	hexane	10.0
8081 (organochlorine pesticides)	5-9	C_{18}	methylene chloride	hexane	10.0
8082 (PCBs)	5-9	C_{18}	methylene chloride	hexane	10.0
8141 (organophosphorus pesticides)	as received	SDB-RPS	MTBE	hexane	10.0
8330 (nitroaromatics and nitramines)	as received	SDB-RPS	acetonitrile	acetonitrile	10.0
8095 (explosives in water)	as received	SDB-RPS	acetonitrile	acetonitrile	5.0
TCLP pesticides (8081)	as produced by TCLP	SDB-XC	ethyl acetate	hexane	10.0
TCLP semivolatiles (8270)	as produced by TCLP	SDB-XC	ethyl acetate	methylene chloride	1.0
TCLP phenoxyacid herbicides (8321)	1.0	SDB-XC	acetonitrile	hexane	10.0

[a] SDB has a greater capacity than C_{18} and a greater affinity for more analytes but they may be more difficult to elute.

[b] For methods where the suggested final extract volume is 10.0 mL, the volume may be reduced to as low as 1.0 mL to achieve lower limits of quantitation. Other final extract volumes may be used, provided that the overall sensitivity meets project-specific needs.

FIGURE 1

EXAMPLE DISK EXTRACTION APPARATUS FOR SINGLE EXTRACTIONS



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ANALYTICAL CHEMISTRY LIST OF CONSTITUENTS

Table 1. List of pesticides to be analyzed in water samples using gas chromatography with mass spectroscopy (GC-MS) and by liquid chromatography (LC) mass spectroscopy mass spectroscopy (MS-MS) by the Organic Chemistry Research Laboratory, Sacramento, California.

GC/MS Compound		CLASS	WATER MDL (ng/L)
3,4-DCA	Degradate	Urea	8.3
3,5-DCA	Degradate	Aniline	7.6
Acibenzolar-S-methyl	Fungicide	Benzothiadiazole	3.0
Alachlor	Herbicide	Chloroacetanilide	1.7
Allethrin	Insecticide	Pyrethroid	6.0
Atrazine	Herbicide	Triazine	2.3
Azoxystrobin	Fungicide	Strobilurin	3.1
Benefin (Benfluralin)	Herbicide	Dinitroaniline	2.0
Bifenthrin	Insecticide	Pyrethroid	4.7
Boscalid	Fungicide	Pyridine	2.8
Butralin	Herbicide	Dinitroaniline	2.6
Butylate	Herbicide	Thiocarbamate	1.8
Captan	Fungicide	Phthalimide	10.2
Carbaryl	Insecticide	Carbamate	6.5
Carbofuran	Insecticide	Carbamate	3.1
Chlorothalonil	Fungicide	Chloronitrile	4.1
Chloroyrifos	Insecticide	Organophosphate	2.1
Chloroyrifos OA	Degradate	Organophosphate	5.0
Clomazone	Herbicide	Isoxazlidinone	2.5
Coumaphos	Insecticide	Oranophosphate	3.1
Cycloate	Herbicide	Thiocarbamate	1.1
Cyfluthrin	Insecticide	Pyrethroid	5.2
Cyhalofop-butyl	Herbicide	Aryloxyphenoxypropionate	1.9
Cyhalothrin	Insecticide	Pyrethroid	2.0
Cypermethrin	Insecticide	Pyrethroid	5.6
Cyproconazole	Fungicide	Thriazole	4.7
Cyprodinil	Fungicide	Pyrimidine	7.4
DCPA	Herbicide	Benzenedicarboxylic Acid	2.0
Deltamethrin	Insecticide	Pyrethroid	3.5
Diazinon	Insecticide	Organophosphate	0.9
Diazinon OA	Degradate	Organophosphate	5.0
Difenoconazole	Fungicide	Triazole	10.5
Dimethomorph	Fungicide	Morpholine	6.0
Dithiopyr	Herbicide	Pyridine	1.6
EPTC	Herbicide	Thiocarbamate	1.5
Esfenvalerate	Insecticide	Pyrethroid	3.9
Ethalfluralin	Herbicide	Aniline	3.0
Etofenorox	Insecticide	Pyrethroid	2.2
Famoxadone	Fungicide	Oxazole	2.5
Fenamidone	Fungicide	Imidazole	5.1

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Fenarimol	Fungicide	Pyrimidine	6.5
Fenbuconazole	Fungicide	Triazole	5.2
Fenhexamide	Fungicide	Anilide	7.6
Fenpropathrin	Insecticide	Pyrethroid	4.1
Fenovroximate	Insecticide	Pyrazole	5.2
Fenthion	Insecticide	Organophosphate	5.5
Fipronil	Insecticide	Phenylpyrazole	2.9
Fipronil desulfinyl	Degradate	Phenylpyrazole	1.6
Fipronil desulfinyl amide	Degradate	Phenylpyrazole	3.2
Fipronil sulfide	Degradate	Phenylpyrazole	1.8
Fipronil sulfone	Degradate	Phenylpyrazole	3.5
Fluazinam	Fungicide	Pyridine	4.4
Fludioxinil	Fungicide	Pyrrole	7.3
Flufenacet	Herbicide	Anilide	4.7
Flumethralin	Plant Growth regulator	Dinitroaniline	5.8
Fluooicolide	Fungicide	Pyrimidine	3.9
Fluoxastrobin	Fungicide	Strobilurin	9.5
Flusilazole	Fungicide	Triazole	4.5
Flutolanil	Fungicide	Anilide	4.4
Flutriafol	Fungicide	Triazole	4.2
Fluxapyroxad	Fungicide	Anilide	4.8
Hexazinone	Herbicide	Triazone	8.4
Imazalil	Fungicide	Triazole	10.5
Indoxacard	Insecticide	Oxadiazine	4.9
Iorodione	Fungicide	Dicarboxamide	4.4
Kresoxim-methyl	Fungicide	Strobilurin	4.0
Malathion	Insecticide	Organophosphate	3.7
Malathion OA	Degradate	Organophosphate	5.0
Metalaxyl	Fungicide	Phenylamide	5.1
Metaconazole	Fungicide	Azole	5.2
Methidathion	Insecticide	Organophosphate	7.2
Methoprene	Insecticide	Terpene	6.4
Methylparathion	Insecticide	Organophosphate	3.4
Metolachlor	Herbicide	Chloroacetanilide	1.5
Molinate	Herbicide	Thiocarbamate	3.2
Myclobutanil	Fungicide	Triazole	6.0
Napropamide	Herbicide	Amide	8.2
Novaluron	Herbicide	Benzoylurea	2.9
Oxadiazon	Herbicide	Oxadiazolone	2.1
Oxyfluorfen	Herbicide	Nitrophenyl ether	3.1
p,p'-DDD	Degradate	Organochlorine	4.1
p,p'-DDE	Degradate	Organochlorine	3.6
p,p'-DDT	Insecticide	Organochlorine	4.0
Paclobutrazol	Fungicide	Triazole	6.2
Pebulate	Herbicide	Thiocarbamate	2.3

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Pendimethalin	Herbicide	Aniline	2.3
Pentachloroanisole (PCA)	Insecticide	Organochlorine	4.7
Pentachloronitrobenzene (PCNB)	Fungicide	Organochlorine	3.1
Permethrin	Insecticide	Pyrethroid	3.4
Phenothrin	Insecticide	Pyrethroid	5.1
Phosmet	Insecticide	Organophosphate	4.4
Picoxystrobin	Fungicide	Strobilurin	4.2
Piperonyl butoxide	Synergist	Unclassified	2.3
Prodiamine	Herbicide	Dinitroaniline	5.2
Prometon	Herbicide	Triazine	2.5
Prometryn	Herbicide	Triazine	1.8
Propanil	Herbicide	Anilide	10.1
Propargite	Insecticide	Sulfite ester	6.1
Propiconazole	Fungicide	Azole	5.0
Propyzamide	Herbicide	Benzamide	5.0
Pyraclostrobin	Fungicide	Strobilurin	2.9
Pyridaben	Insecticide	Pyridazinone	5.4
Pyrimethanil	Fungicide	Pyrmidine	4.1
Quinoxyfen	Fungicide	Quinoline	3.3
Resmethrin	Insecticide	Pyrethroid	5.7
Simazine	Herbicide	Triazine	5.0
Tebuconazole	Fungicide	Azole	3.7
Tebupirimfos	Insecticide	Organophosphate	1.9
Tebupirimfos OA	Degradate	Organophosphate	2.8
Tefluthrin	Insecticide	Pyrethroid	4.2
Tetraconazole	Fungicide	Azole	5.6
Tetradifon	Insecticide	Bridged diphenyl	3.8
Tetramethrin	Insecticide	Pyrethroid	2.9
t-fluvalinate	Insecticide	Pyrethroid	5.3
Thiazopyr	Herbicide	Pyridine	4.1
Thiobencarb	Herbicide	Thiocarbamate	1.9
Triadimefon	Fungicide	Triazole	8.9
Triadimenol	Fungicide	Triazole	8.0
Triallate	Herbicide	Carbamate	2.4
Tribufos	Herbicide	Organophosphate	3.1
Trifloxystrobin	Fungicide	Strobilurin	4.7
Triflumizole	Fungicide	Azole	6.1
Trifluralin	Herbicide	Aniline	2.1
Triticonazole	Fungicide	Azole	6.9
Zoxamide	Fungicide	Benzamide	3.5
LC-MC/MS (Compound)		**CLASS**	**WATER MDL (ng/L)**
Acetamiprid	Insecticide	Neonicotinoid	3.6
Clothianidin	Insecticide	Neonicotinoid	6.2

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ANALYTICAL CHEMISTRY LIST OF CONSTITUENTS

Dinotefurn	Insecticide	Neonicotinoid	5.5
Imidacloprid	Insecticide	Neonicotinoid	4.9
Thiacloprid	Insecticide	Neonicotinoid	3.8
Thiamethoxam	Insecticide	Neonicotinoid	3.9
3,4-DCA (diuron degradate)	Degradate	Urea	5.2
DCPU (diuron degradate)	Degradate	Urea	4.3
DCPMU (diuron degradate)	Degradate	Urea	3.0
Diuron	Herbicide	Urea	3.2

Procedures and Methods

Pre-Deployment Conditioning of Disks and Membranes

Disks and diffusion limiting membranes (DLMs) were conditioned prior to deployment. Horizon Atlantic HLB disks were cleaned/conditioned with two 10 mL aliquots of methanol (MeOH) followed by two aliquots of organic free distilled water (OFW). Empore SDB-RPS disks were cleaned with 10 mL acetone (ACE) then 10 mL isopropyl alcohol (IPA) and conditioned with 10 mL of MeOH followed by two 10 mL aliquots of OFW. Disks were not allowed to go dry during the conditioning process. A 10 mL aliquot of OFW was spiked with recovery surrogate standards, monuron, d_4-imidacloprid, $^{13}C_3$-atrazine, ring-$^{13}C_{12}$-*p,p'*- DDE and di-*N*-propyl-d_{14}-trifluralin, phenoxy-$^{13}C_6$-*cis*-permethrin and $^{13}C_4$-fipronil and loaded into each disk.

DLMs were cleaned prior to use. Low density polyethylene (LDPE) were soaked in hexane overnight then placed in OFW until needed. Microporous polysulfone (PES) membranes were soaked overnight in MeOH then placed if OFW until needed.

The surrogate spiked preconditioned Atlantic HLB disks were placed in a Chemcatcher holders, if needed a pre-cleaned LDPE membrane was placed on top the disk, capped, and the assemblies were kept chilled at -20˚C until deployment. The surrogate spiked preconditioned Empore SDB-RPS disks were placed in the holders. A pre-cleaned PES membrane was placed on the surface if needed. To prevent the accumulation of ice crystals that may cause tearing, the Empore SDB-RPS disks were kept at 2˚C until deployment.

Disk Processing and Analytical Methods

Upon retrieval Horizon Atlantic disks were stored at –20°C and Empore SDB-RPS disks were stored at 2°C until they were extracted. Elution occurred within 7 days of reaching the laboratory. The sorbent disks were removed from the housing and either dried on a vacuum manifold or in a freeze drier. Once dry, the disks were eluted twice with 10 mL aliquots of 1:1 methanol (MeOH) and acetonitrile (ACN) using an ENVI® disk holder at a rate 5 mL/minute. The eluent was evaporated to 1.0 mL in an accelerated evaporator under nitrogen then split equally into two fractions. Each fraction was solvent-exchanged by adding either ethyl acetate (EtOAc; fraction 1) or ACN (fraction 2). If residual water was present in the sample they were dried using sodium sulfate (Na_2SO_4). The samples were then evaporated using a gentle stream of nitrogen to 0.2 mL. An internal standard was added to each fraction. Fraction 1 received 20uL of a 10ng/µL internal standard solution containing the deuterated polycyclic aromatic hydrocarbon compounds acenaphthene-d_{10}, phenanthrene d_{10}, and pyrene-d_{10} and fraction 2 received 20 µL of a 5-ng/µL solution d_3-chlothianidin. Samples were stored in a freezer at –20°C until analysis (up to 30 days).

GC/MS Method:

GC conditions: Separation was done on an Agilent 7890A GC coupled to a 5975C MS system operated in electron impact (EI) mode. Injections of 1 µL are made with the injector at 275ºC in pulsed splitless mode with a 50 psi pressure pulse for 1 min. The flow of helium through a DB-5 (30 m x 0.25 mm x 0.25 um) GC column is set at 1.2 mL/min. The Injection 1 oven program is 80ºC for 1.0 min, ramp at 10ºC/min until 120ºC, then ramp at 3ºC/min until 200ºC and hold for 5 minutes, ramp at 3ºC/min until 219ºC, and a final ramp at 10ºC/min until 300ºC and hold for 10 minutes. The Injection 2 oven program is 80ºC for 0.5 min, ramp at 10ºC/min until 180ºC, then ramp at 5ºC/min until 220ºC and hold

for 1 minute, ramp at 4ºC/min until 280ºC and hold for 1 minute, and a final ramp at 10ºC/min until 300ºC and hold for 10 minutes.

MS Conditions: the transfer line from the GC to the MS is set at 280ºC, the quadrupole is at 150ºC, and the MS ion source is set at 230ºC. The MS is operated in electron-ionization (EI) mode. Data is collected in the selected-ion-monitoring (SIM) mode; details of the retention times, quantitation ions, and qualification ions for the SIM windows are given in the provided spreadsheet (Table 1).

LCMSMS Method:

Aliquots of the samples (10 µL) are injected, and the compounds, separated on an Agilent 1260 HPLC coupled to a 6430 tandem MS system with a Zorbax Eclipse XDB-C18 column (2.1 mm × 150 mm × 3.5 mm; Agilent). The column flow rate is 0.6 mL/min, and the column temperature us 30°C. The mobile phases are ACN (A channel) and 5 millimoloar (mM) formic acid in water (B channel). The column gradient is 2 percent: 98 percent (A:B) from 0 to 2 min; 2 to 4 min increase to 50 percent : 50 percent (A:B), hold for 3 min (7 min); 7 to 7.5 min decrease to 2 percent : 98 percent (A:B), hold for 4.5 min (12 min). MS/MS conditions are electrospray (ESI) ionization, positive mode, drying gas temperature 350°C, drying gas flow 10 L/min, capillary voltage 4,000 V, and nebulizer 40 psi. Data are collected in the multiple-reaction-monitoring (MRM) mode; details of the MRM parameters are given in the provided spreadsheet. Most compounds are run in ESI+ mode, however, two compounds are done in ESI- mode as noted in the spreadsheet (Table 2).

Aquatic Passive Sampling via Solid-Phase Extraction Media for Cannabis and Timber Cultivation Pesticides in Northern California

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Introduction

Cannabis production in Northern California mountain and foothill regions has increased dramatically over the last decade. Pesticides (including pesticides banned in the U.S.) are used by unlicensed applicators during cannabis production and their use is completely unregulated (Mallery, 2011). Pesticides are also applied in these same regions during commercial timber production and for right-of-way maintenance. Thousands of pounds of forestry pesticides and an unknown amount of cannabis production pesticides are applied on thousands of acres of forested and foothill regions and within multiple watersheds per year (California Department of Pesticide Regulation, 2017). There are no existing data or monitoring programs for surface water discharges of cannabis or forestry pesticides in these regions. These pesticides may pose a threat to aquatic organisms, including State and Federal *special status* species (*e.g.*, salmonids) in surface waters downstream of these sources.

Passive sampling techniques are becoming more popular as a monitoring tool to detect episodic pulses of contaminants in water. They also offer the ability to concentrate compounds over time and in larger volumes of water that would otherwise be below method detection limits in a traditional one liter water grab sample. In addition, monitoring programs using traditional sampling techniques such as grab samples collected at a fixed sampling interval would likely lack the temporal resolution to detect episodic and fluctuating discharges of pesticides. By extracting in situ, passive sampling reduces the need to provide large volumes of water to a laboratory and therefore reduces labor and shipping costs. These attributes make passive sampling for pesticides very attractive for non-point source screening and monitoring.

The Chemcatcher® passive sampling device was selected for this study. This device utilizes solid phase extraction media (SPE) in the form of commercially available disks that include different SPE media types. Solid phase extraction is the technique of choice for extraction, concentration, and clean-up of traditional

grab samples because it allows for the concentration of target analytes while minimizing background interferences to provide low detection levels needed in aquatic sampling. The benefits of passive sampling and solid phase extraction are combined in the Chemcatcher® resulting in the ability to detect low levels of contaminants. Multiple types of SPE sorbent disks can be used in one device allowing for the extraction of a wide range of pesticides with different chemical structures and functional groups. For this study, Atlantic® hydrophilic-lipophilic balance (HLB) and Empore™ styrene divinylbenzene reverse phase sulfonate (SDB-RPS) disks were chosen to target a large suite of pesticides. The Atlantic® HLB should perform well in extracting both hydrophobic (log K_{ow}>3) and hydrophilic (log K_{ow}<3) organic compounds while the Empore™ SBD-RPS should perform better for extracting hydrophilic compounds (Vrana and others, 2006). Both SPE disk types can be used with or without a diffusion limiting membrane (DLM). DLMs reduce biofouling by providing a semipermeable barrier between the SPE sorbent media and the aqueous environment (Vrana and others, 2006). The non-porous low density polyethylene (LDPE; log K_{ow} >3-4) DLM was combined with the Atlantic® HLB and the microporous polyethersulfone (PES; log K_{ow} <3) DLM was combined with the Empore™ SDB-RPS for longer deployment times (>14 d).

This study is a pilot project that assessed the occurrence of a large suite of current-use pesticides and pesticide degradates in surface waters in Northern California. Results from this study will be used by the Central Valley Regional Water Quality Control Board (Central Valley Water Board) and other resource managers to assess the potential impact of pesticides on aquatic *special status* species.

Study Design

Passive samplers (Chemcatcher®) were deployed in the Upper Sacramento River downstream of cannabis and/or commercial timber production areas during the fall of 2016 and in Little Cow Creek and Deer Creek in the summer of 2017. Samplers were deployed during two storm events for 24 hours in the fall of 2016 and twice during mid-summer 2017 (21 and 23 days respectively) prior to retrieval. Chemcatchers® were deployed with commercially available 47 mm diameter solid-phase extraction (SPE) disks. Short duration (24 hr) samples were obtained without the use of a diffusion limiting membrane (DLM) while longer duration samples (~22 d) were deployed with a DLM.

Upon retrieval the samplers were processed and analyzed for a suite of over 150 current-use pesticides and degradates by gas chromatography tandem mass spectrometry (GC-MS/MS) and liquid chromatography tandem mass spectrometry (LC-MS/MS).

In addition to a previously developed list of compounds, the pesticides aminopyralid, 2,4-D, metaldehyde, methamidophos, strychnine, sulfometuron methyl, and triclopyr were tested for possible inclusion in the analytical methods. A laboratory spike experiment was conducted to evaluate the efficiency of disks for the extraction of the target list of pesticides.

Site Locations

Sampling sites were selected that were downstream from a mixture of timber production, cannabis grow sites, and transmission corridors located in Northern California (**Figure 1**). Land use for the sites was determined by evaluating the Cal Fire Forest Water Shed Mapper (http://egis.fire.ca.gov/watershed_mapper/), California Energy Commission Energy Maps of California (http://www.energy.ca.gov/maps/), and Google Earth. Additional information provided by the Central Valley Water Board Cannabis Regulatory Enforcement Unit and California Department of Fish and Wildlife law enforcement was used to confirm the presence of cannabis cultivation activity. The field sites and dates deployed are shown in **Table 1**. The Upper Sacramento River was sampled twice in the fall for 24 hr. and both Little Cow Creek and Deer Creek were sampled in the summer for 21 and 23 days respectively.

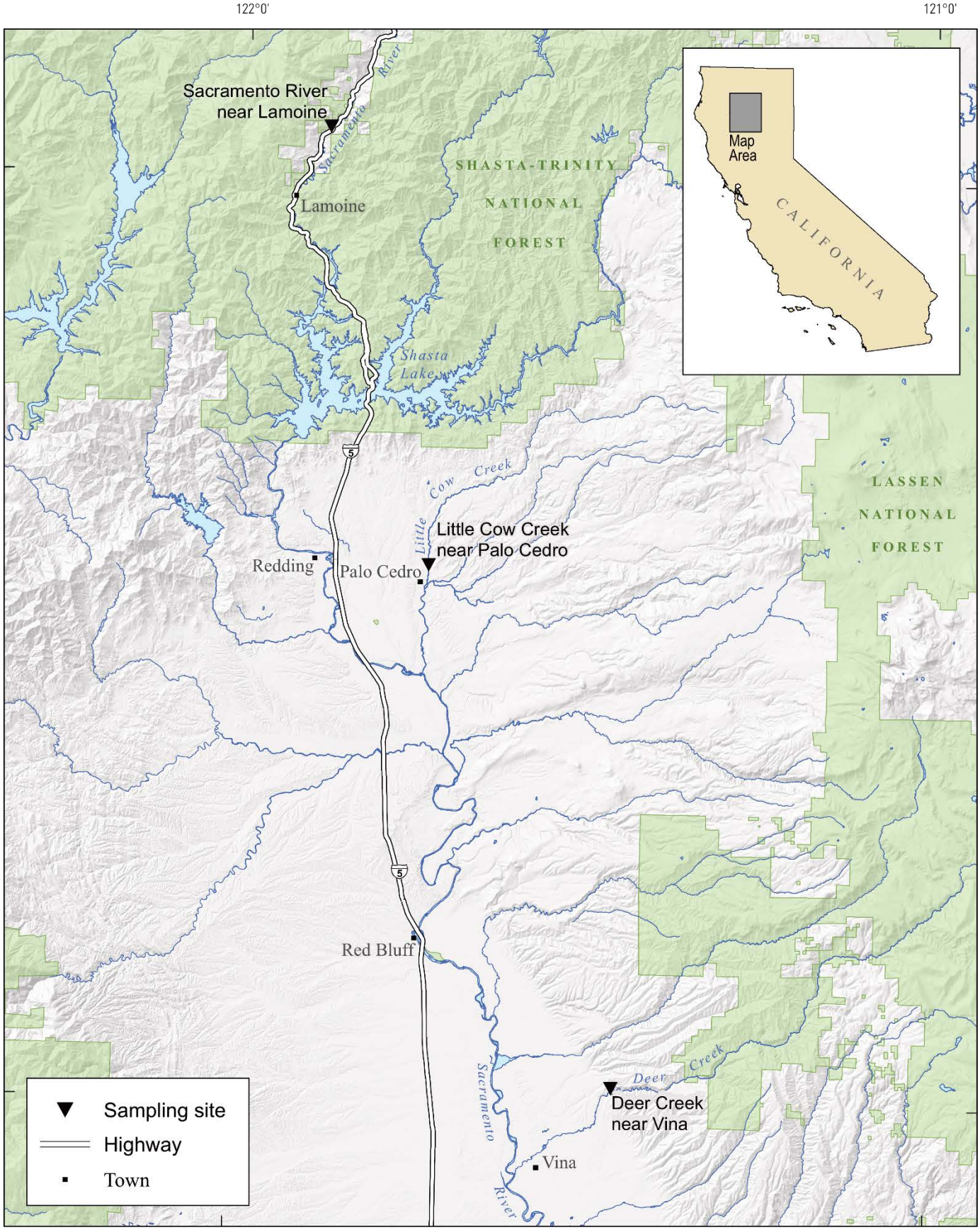

Figure 1. Sampling site location

Table 1. Sampling sites and deployment dates. Calif., California; USGS, U.S. Geological Survey; [d, days; hr, hours; °, degrees; ', minutes; ", seconds]. [1]All locations reference North American Datum 1983.

USGS station number	USGS station name	Field ID	Latitude[1] (dms)	Longtitude[1] (dms)	Season	Deployment dates	Duration of deployment
11383500	Deer Creek near Vina, Calif.	Deer Creek	40° 00' 51"	121° 56' 54"	Summer	07/24/2017-08/16/2017	23 d
403434122133301	Little Cow Creek near Palo Cedro, CA	Little Cow Creek	40° 34' 34"	122° 13' 33"	Summer	07/27/2017-08/17/2017	21 d
410252122225301	Sacramento River near Lamoine, California	Upper Sacramento River	41° 02' 52"	122° 22' 53"	Fall	10/17/2016-10/18/2016	24 hr
410252122225301	Sacramento River near Lamoine, California	Upper Sacramento River	41° 02' 52"	122° 22' 53"	Fall	10/26/2016-10/27/2016	24 hr

Procedures and Methods

Pre-Deployment Conditioning of Disks and Membranes

Disks and DLMs were conditioned prior to deployment. Horizon Atlantic® HLB disks were cleaned/conditioned with two 10 mL aliquots of methanol (MeOH) followed by two aliquots of organic free distilled water (OFW). Empore™ SDB-RPS disks were cleaned with 10 mL acetone (ACE) then 10 mL isopropyl alcohol (IPA) and conditioned with 10 mL of MeOH followed by two 10 mL aliquots of OFW. Disks were not allowed to go dry during the conditioning process. A 10 mL aliquot of OFW was spiked with recovery surrogate standards (monuron, d_4-imidacloprid, $^{13}C_3$-atrazine, ring-$^{13}C_{12}$-*p,p'*- Dichlorodiphenyldichloroethylene (*p,p'*-DDE), di-*N*-propyl-d_{14}-trifluralin, phenoxy-$^{13}C_6$-*cis*-permethrin and $^{13}C_4$-fipronil) and loaded into each disk. DLMs were cleaned prior to use. Low density polyethylene (LDPE) DLMs were soaked in hexane overnight then placed in OFW until needed. Microporous polysulfone (PES) membranes were soaked overnight in MeOH then placed in OFW until needed.

The surrogate spiked preconditioned Atlantic® HLB disks were placed in a Chemcatcher® holder, if needed a pre-cleaned LDPE membrane was placed on top of the disk, the assembly was capped, and kept chilled at -20 °C until deployment. The surrogate spiked preconditioned Empore™ SDB-RPS disks were placed in the holders in the same manner, a pre-cleaned PES membrane was placed on the disk surface if needed. To prevent the accumulation of ice crystals that could cause tearing, the Empore™ SDB-RPS disks were kept at 2 °C until deployment. The preconditioned SPE disks were then shipped with ice, via overnight mail, to and from the USGS Lab (Sacramento) to the Central Valley Water Board Office in Redding.

Field Deployment Procedures

SPE disks were taken to the field on ice. Before attaching the SPE disk holders inside of the Chemcatcher housing, the housing was placed in the stream for about 10 minutes to ensure any cleaning residues were rinsed off. The sample holders were then placed in the Chemcatcher® housing with the surface of the disks oriented down to reduce sediment build-up on the face of the disk. They were secured with cotter pins and the caps were removed. The housing was placed in the stream under water, ensuring the device would not be exposed to the air during the entire deployment time.

Upon retrieval the sample holders containing the disks were removed from the Chemcatcher® housing and capped. The capped samples were wrapped in aluminum foil, placed in sealed plastic bags, and placed on ice for the short (generally one hour) transport to the Redding office. After returning to the office, samples were packed in small cardboard shipping boxes (with small ice packs), and kept in a separate cooler (with separate ice for the cooler) until mailing pickup later that afternoon. At the time of mailing pickup, only the small cardboard shipping box was transported via FedEx overnight to the USGS lab in Sacramento.

Disk Processing and Analytical Methods

Upon receipt at the laboratory the Atlantic® HLB disks were stored in a freezer at -20 °C and the Empore™ SDB-RPS disks were stored in a refrigerator at 4 °C until they were eluted. Elution occurred within 7 d of reaching the laboratory. The sorbent disks were removed from the housing and either dried on a vacuum manifold or in a freeze drier. Once dry, the disks were eluted twice with 10 mL aliquots of 1:1 methanol (MeOH) and acetonitrile (ACN) using an ENVI® disk holder at a rate 5 mL/min. The eluent was evaporated to 1.0 mL in an accelerated evaporator under nitrogen and then split into two equal fractions. Each fraction was solvent-exchanged by adding either ethyl acetate (EtOAc; fraction 1) or ACN (fraction 2). If residual water was present in the extract they were dried using sodium sulfate (Na_2SO_4). The extracts were then evaporated using a gentle stream of nitrogen to 0.2 mL. An internal standard was added to each fraction. Fraction 1 received 20 µL of a 10 ng/µL internal standard solution containing deuterated polycyclic aromatic hydrocarbon compounds (d_{10}-acenaphthene,d_{10}-phenanthrene, and d_{10}-pyrene) and fraction 2 received 20 µL of a 5-ng/µL solution of d_3-chlothianidin. Sample extracts were stored in a freezer at -20 °C until analysis (up to 30 d).

GC-MS and GC-MS/MS Method:

Separation for the laboratory spike samples was done on an Agilent 7890A GC coupled to a 5975C MS system. Separation for the environmental samples (fraction 1) was done on an Agilent 7890A GC coupled to a 7000 MS/MS system. Both systems were operated in electron impact (EI) mode. Injections of 1 µL were made with the injector at 275 °C in pulsed splitless mode with a 50 psi pressure pulse for 1 min. The flow of helium through the DB-5 (30 m × 0.25 mm × 0.25 µm) GC column was set at 1.2 mL/min. Each sample was injected in two different temperature programs. The Injection 1 oven program was 80 °C for 1.0 min, ramp at 10 °C/min until 120 °C, then ramp at 3 °C/min until 200 °C and hold for 5 min, ramp at 3 °C/min until 219 °C, and a final ramp at 10 °C/min until 300 °C and hold for 10 min. The Injection 2 oven program was 80 °C for 0.5 min, ramp at 10 °C/min until 180 °C, then ramp at 5 °C/min until 220 °C and hold for 1 min, ramp at 4ºC/min until 280 °C and hold for 1 min, and a final ramp at 10 °C/min until 300 °C and hold for 10 mins. The transfer line for the GC-MS system was set at 280 °C, the quadrupole was at 150 °C, and the MS ion source was set at 230 °C. The transfer line for the GC-MS/MS system, from the GC to the MS/MS, was set at 300 °C, the quadrupole was at 150 °C, and the MS ion source was set at 230 °C. The MS was operated in Selective Ion Monitoring Mode (SIM) and the MS/MS in Multiple Reaction Mode (MRM). More information on the GC-MS analysis can be obtained from (Hladik and others, 2008 and 2009; Hladik and McWayne, 2012).

LC-MS/MS Method:

Aliquots of the environmental sample (10 µL of fraction 2) were injected and the compounds separated on an Agilent 1260 HPLC coupled to a 6430 tandem MS system with a Zorbax Eclipse XDB-C18 column (2.1 mm × 150 mm × 3.5 mm; Agilent). The column flow rate was 0.6 mL/min, and the column temperature was 30 °C. The mobile phases were ACN (A channel) and 5 millimolar (mM) formic acid in water (B channel). The column gradient was 2 percent: 98 percent (A:B) from 0 to 2 min; 2 to 4 min increase to 50 percent: 50 percent (A:B), hold for 3 min (7 min); 7 to 7.5 min decrease to 2 percent: 98 percent (A:B), hold for 4.5 min (12 min). MS/MS conditions were electrospray (ESI) ionization, positive or negative mode, drying gas temperature 350 °C, drying gas flow 10 L/min, capillary voltage 4,000 V, and nebulizer 40 psi. Data were collected in the multiple-reaction-monitoring (MRM) mode. More information about the LC-MS/MS instrumental analysis can be obtained from (Hladik, M.L. and Calhoun, D.L., 2012).

Method Performance Issues

Initially the disks were dried on a manifold, eluted with MeOH, and exchanged into ACN for analysis. Low internal standard response was seen in the first data set acquired by GC-MS/MS and samples had to be dried further with sodium sulfate. To improve method drying, future samples were freeze dried, eluted, and then exchanged into ethyl acetate (immiscible with water) prior to GC-MS/MS analysis. If needed, further drying was done by the addition of sodium sulfate. Internal standard response improved with these method adjustments.

Surrogate recovery for many samples were low (<70%) for both disk types from the first deployment as shown in **Table 2**. Initially disks were spiked by adding the surrogate solution to the surface of each disk after conditioning. After the first data set uniformly resulted in poor recovery, surrogate addition was modified. After the conditioning step, future samples were spiked by running 10 mL of OFW that had been spiked with the recovery surrogates through the disks using the ENVI disk holder. Recovery did not improve for all compounds, some compounds saw improvement while others had lower recoveries. However, more consistency between samples and their corresponding replicates was seen. It is important to note that surrogate compounds may diffuse out of the sorbent disks during deployment. The amount of diffusion is dependent on a complex set of factors including affinity for the sorbent disk and hydrologic conditions, therefore, we don't anticipate surrogate recoveries to be above 70% for the surrogate compounds. However, further modifications are being done in an attempt to improve surrogate loading to allow for more consistency in surrogate recovery.

Table 2. Percent recovered of labeled surrogate compounds for each disk. Values are in percent (%). Disks were spiked before deployment.

Site Name	Dates	Type	Sorbent	$^{13}C_3$-Atrazine	$^{13}C_{12}$-*p,p'*-DDE	$^{13}C_4$-Fipronil	d_4-Imida-cloprid	Monuron	$^{13}C_6$-*cis*-permethrin	d_{14}-Trifluralin
Upper Sacramento	10/17/16-10/18/16	Environ	HLB	27	6	5	22	25	7	4
Upper Sacramento	10/17/16-10/18/16	Replicate	HLB	17	3	1	17	19	2	1
Upper Sacramento	10/17/16-10/18/16	Environ	SDB-RPS	23	28	29	29	21	57	17
Upper Sacramento	10/17/16-10/18/16	Replicate	SDB-RPS	40	39	34	31	25	75	28
Upper Sacramento	10/17/16-10/18/16	Replicate	HLB	45	15	22	21	24	56	7
Upper Sacramento	10/26/16-10/27/16	Environ	HLB	45	5	19	13	16	28	11
Upper Sacramento	10/26/16-10/27/16	Replicate	HLB	84	7	32	10	7	26	16
Upper Sacramento	10/26/16-10/27/16	Environ	SDB-RPS	77	55	79	57	45	83	64
Upper Sacramento	10/26/16-10/27/16	Replicate	SDB-RPS	81	59	64	39	28	80	65

Deer Creek	07/24/17-08/16/17	Environ	HLB	65	17	15	36	46	24	21
Deer Creek	07/24/17-08/16/17	Replicate	HLB	101	16	45	44	54	26	18
Deer Creek	07/24/17-08/16/17	Environ	SDB-RPS	115	25	80	42	41	47	27
Deer Creek	07/24/17-08/16/17	Replicate	SDB-RPS	111	15	67	42	38	30	21
Little Cow Creek	07/27/17-08/17/17	Replicate	SDB-RPS	66	40	73	39	44	64	31
Little Cow Creek	07/27/17-08/17/17	Environ	HLB	64	11	13	29	39	22	14
Little Cow Creek	07/27/17-08/17/17	Replicate	HLB	83	12	35	47	62	22	14
Little Cow Creek	07/27/17-08/17/17	Environ	SDB-RPS	66	12	52	43	48	24	12
Little Cow Creek	07/27/17-08/17/17	Replicate	SDB-RPS	91	14	68	44	45	28	16

Laboratory Spike Experiment

The water for the laboratory spike test was obtained as a grab sample from the American River near Guy West Bridge. The water was filtered through baked 0.7 µm glass fiber filters (GF/F) prior to spiking and extraction. Extraction disks were preconditioned and spiked with surrogates in the same manner as previously described for the field study. No membranes were used. The filtered water was divided into 1 liter samples that were spiked with the target analytes (100 µL of 2ng/L stock solutions). Each disk type (HLB or SDB-RPS) was tested in triplicate with an additional fourth sample extracted as a background blank. Each 1-L water sample was extracted through a disk at the rate of approximately 10 mL/minute using the ENVI-disk holder and a small vacuum pump. After the sample was extracted the disks were freeze dried, eluted, concentrated, spiked with internal standard, and analyzed as previously described for the field study except the laboratory spike samples were not split into fractions. Instead they were exchanged into ACN only and reduced to 0.2 mL. The sample then received both internal standards the one sample extract was analyzed by each instrument.

Results and Conclusions

Field Study

The pesticides detected in the environmental samples, measured in ng/disk, are shown in **Table 3** and the detection frequency of each pesticide is shown in **Figure 2.** The total number of detections was 35. The compounds detected included the herbicides dacthal (DCPA) dithiopyr, hexazinone, and trifluralin. Also detected were the insecticide *p,p'*-DDE and the fungicides chlorothalonil, imazalil, and thiabendazole. A wider variety of

pesticides were detected in the fall deployment but the frequency of detection in the summer (54%) was higher than in the fall (37%). Chlorothalonil was not detected in the Upper Sacramento River but was detected in both Little Cow Creek and Deer Creek. All the pesticides detected in Little Cow Creek were also detected in Deer Creek.

Most the detections (80%) were only seen in the Empore™ SDB-RPS disks for the majority of the compounds detected indicating that the disk may perform better in the field than the Atlantic® HLB for the target list of compounds. Trifluralin was the most frequently detected pesticide and was detected in 56% of the samples. The Empore™ SDB-RPS disk detected 36% of the total trifluralin detection while the Atlantic® HLB detected 17%. Dithiopyr and hexazinone were the second most detected pesticides with a total detection frequency of 39% and 36% respectively. Dithiopyr was detected in 39% of the samples with most detections made by the SDB-RPS (28%) compared to the HLB (11%). The compounds DCPA, imazalil, and thiobendazole only had one detection throughout the study. Due to the small number of pesticide detections overall, which may not be abnormal in these streams, more testing was conducted to further evaluate the disks effectiveness for pesticide sorption.

Table 3. Pesticide concentrations (ng/disk) fall and summer. Each site had at least two HLB and two SDB-RPS disks deployed at the same time. ND = not detected. Total detection is the number of disks resulting in a positive detection with F denoting Fall and S denoting Summer deployment.

Location	Dates	Sorbent Type	Sample Type	DLM	Chlorothal-onil	DCPA	*p,p'*-DDE	Dithiopyr	Hexazi-none	Imazalil	Thiabend-azole	Triflur-alin
Upper Sacramento	10/17/16-10/18/16	HLB	Environ	none	ND	ND	ND	ND	ND	ND	ND	ND
Upper Sacramento	10/17/16-10/18/16	HLB	Replicate	none	ND	ND	ND	ND	ND	ND	ND	ND
Upper Sacramento	10/17/16-10/18/16	HLB	Replicate	none	ND	ND	ND	ND	ND	ND	ND	ND
Upper Sacramento	10/17/16-10/18/16	SDB-RPS	Environ	none	ND	ND	ND	ND	ND	ND	6	ND
Upper Sacramento	10/17/16-10/18/16	SDB-RPS	Replicate	none	ND	ND	ND	ND	18	ND	ND	ND
Upper Sacramento	10/26/16-10/27/16	HLB	Environ	none	ND	ND	ND	11	ND	33	ND	ND
Upper Sacramento	10/26/16-10/27/16	HLB	Replicate	none	ND	ND	12	14	ND	ND	ND	13
Upper Sacramento	10/26/16-10/27/16	SDB-RPS	Environ	none	ND	9	9	10	18	ND	ND	20
Upper Sacramento	10/26/16-10/27/16	SDB-RPS	Replicate	none	ND	ND	11	12	21	ND	ND	16
Deer Creek	07/24/17-08/16/17	HLB	Environ	LDPE	ND	ND	ND	ND	ND	ND	ND	ND
Deer Creek	07/24/17-08/16/17	HLB	Replicate	LDPE	ND	ND	ND	ND	ND	ND	ND	5
Deer Creek	07/24/17-08/16/17	SDB-RPS	Environ	PES	23	ND	ND	6	5	ND	ND	27
Deer Creek	07/24/17-08/16/17	SDB-RPS	Replicate	PES	8	ND	ND	5	ND	ND	ND	27

Little Cow Creek	07/27/17-08/17/17	HLB	Environ	LDPE	ND	ND	ND	ND	ND	ND	ND	ND
Little Cow Creek	07/27/17-08/17/17	HLB	Replicate	LDPE	ND	ND	ND	ND	ND	ND	ND	7
Little Cow Creek	07/27/17-08/17/17	SDB-RPS	Environ	PES	14	ND	ND	ND	21	ND	ND	15
Little Cow Creek	07/27/17-08/17/17	SDB-RPS	Replicate	PES	26	ND	ND	ND	38	ND	ND	13
Little Cow Creek	07/27/17-08/17/17	SDB-RPS	Replicate	PES	15	ND	ND	19	46	ND	ND	19
# of detections					**5S**	**1F**	**3F**	**4F;3S**	**3F;4S**	**1F**	**1F**	**3F;7S**

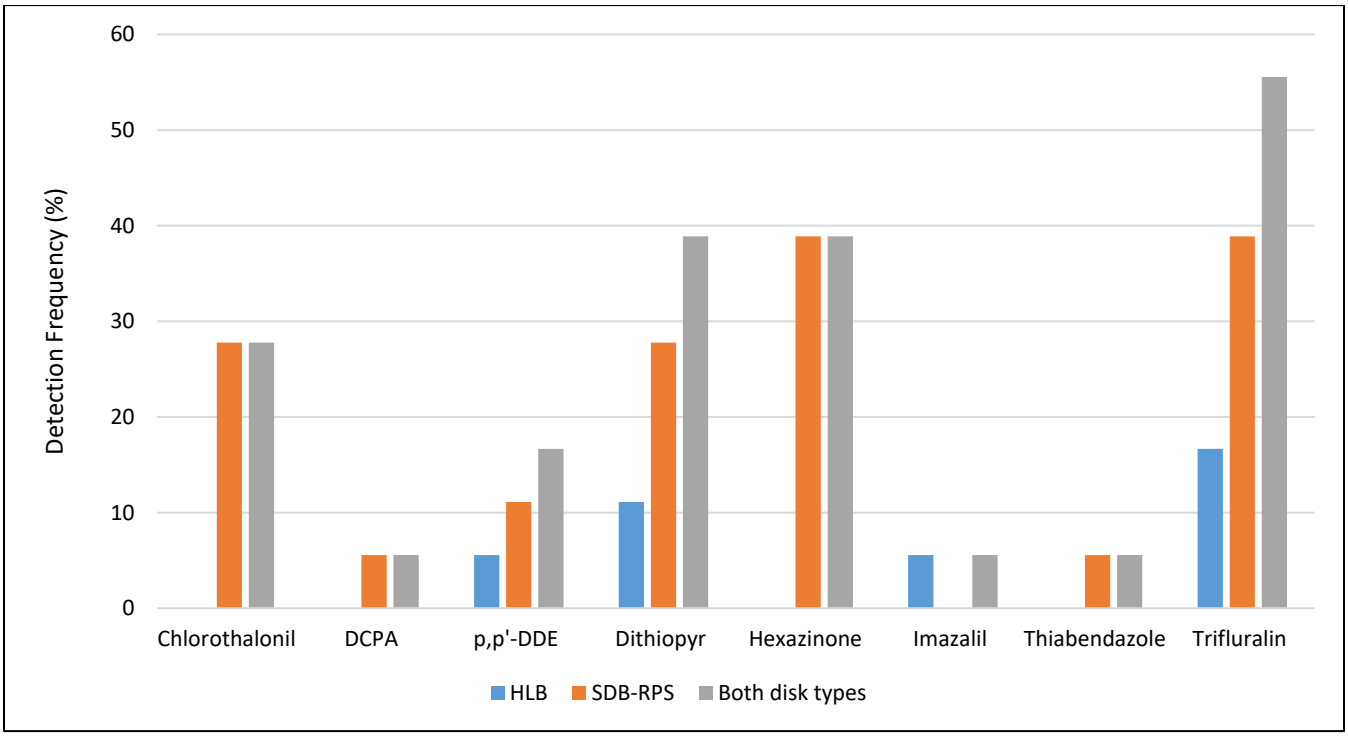

Figure 2. Detection frequency measured in percentage (%). The 1st (blue) bar represents Atlantic® HLB disks, the 2nd (orange) represents Empore™ SDB-RPS disks, and the 3rd (gray) bar represents total detections including both disks types.

Most of the compounds detected are widely used and are not specific to timber production, cannabis, or even rights of way maintenance (a common use of herbicides) however the herbicides dithiopyr, hexazinone and trifluralin are approved for commercial forestry. There is no available application or monitoring data for illegal cannabis cultivation and it is suspected that a wide range of compounds are being used in unknown quantities. Trifluralin and dithiopyr are typically used to control pre-emergent grasses while hexazinone is a broad class herbicide. The compound *p,p'*-DDE is a break down product of the historically used insecticide DDT. Two of the fungicides, imazalil and thiabendazole, are approved for use for specific crops such as citrus but they also have veterinary uses in the treatment of livestock. Chlorothalonil is a broad spectrum fungicide commonly used for

peanuts and tomato crops which are not commonly grown in large scale in the study area. The detections of the fungicides chlorothalonil, imazalil and thiabendazole which are not used in commercial forestry operations (Department of Pesticide Regulation, 2017) may indicate use of these pesticides on cannabis upstream of our deployment site.

It may be important to note that the year this study was conducted was atypical with a very wet rainy season that yielded higher than expected flows for the field sites during storm sampling (fall 2016 sampling events on the Upper Sacramento River). This may have affected passive sampling as the sampling kinetics are influenced by flow. Also rains during the study year extended further into the spring than is typical. This changed our sampling strategy from a spring deployment to a summer deployment.

Laboratory Study

The laboratory spike test yielded compound recoveries **(Table 4)** that were of an acceptable range if the percent recovery fell between 70-130%. Both the Atlantic® HLB and Empore™ SDB-RPS showed acceptable recovery for the majority of the compounds tested. The Empore™ SDB-RPS disks had higher recovery values when analyzed on the GC-MS than Atlantic® HLBs, this could be from better extraction performance by the disk media or matrix enhancement. However, the SDB-RPS had slightly lower recovery than the HLB for many compounds when analyzed by LC-MS/MS. In the Injection 1 program, the compound prometon did not have a response that could be distinguished from background. The compound 3,5-DCA had poor recovery using both disks but was detectable. Malaoxon, methyl parathion and tau-fluvalinate did not perform well (low recovery <70%) using the Atlantic® HLB disk however all their recoveries using the SDB-RPS disk were acceptable. In the Injection 2 program, the compound chlorothalonil had poor recoveries using the Atlantic® HLB disk and novaluron did not perform well when extracted by both disk types with both low response and bad peak shape. Pyraclostrobin performed inconsistently with the Empore™ SDB-RPS due to background interference but performed well with the Atlantic® HLB disk.

Recoveries were lower overall for LC-MS/MS compounds for both the HLB and SDB-RPS disks. This could be due to poorer performance with these compounds or due to the laboratory spike loading method which does not mimic field extraction ideally. The compounds cyazofamid, dinotefuran, flupyradifurone, oryzalin,

penthiopyrad, and thiacloprid had low recoveries (<70%) using the HLB disk. The compounds dinotefuran, flonicamid, oryzalin, and penoxsulam had low recoveries (<70%) using the SDB-RPS disk.

Table 4. Compounds analyzed for GC-MS/MS and LC/MS/MS Methods. 1 and 2 denote injection. ND = not detected.

Pesticide	Chemical class	Pesticide type	Analytical method	HLB (% Rec)	Std. Dev.	SDB-RPS (% Rec)	Std. Dev.
2,4-Dichlorophenoxyacetic	Chlorophenoxy	Herbicide	LC-MS/MS	11	1	ND	ND
3,4-Dichloroaniline	Amine	Degradate	LC-MS/MS	124	12	117	12
3,5-Dichloroaniline	Unclassified	Degradate	GC-MS:1	66	17	61	6
Acetamiprid	Neonicotinoid	Insecticide	LC-MS/M	76	4	82	16
Acibenzolar-S-methyl	Unclassified	Fungicide	GC-MS:2	97	15	118	14
Allethrin	Pyrethroid	Insecticide	GC-MS:1	92	8	111	6
Aminopyralid	Pyridine carboxylic acid	Herbicide	LC-MS/MS	ND	ND	ND	ND
Atrazine	Triazine	Herbicide	GC-MS:1	102	11	115	7
Azinphos-methyl	Organophosphorus	Insecticide	GC-MS:1	87	17	92	15
Azinphos-methyl oxon	Organophosphorus	Degradate	GC-MS:1	107	17	111	12
Azoxystrobin	Strobin	Fungicide	GC-MS:2	92	26	107	26
Benefin (Benfluralin)	2,6-Dinitroaniline	Herbicide	GC-MS:1	72	7	92	7
Benzovindiflupyr	Pyrazolecarboxamide	Fungicide	GC-MS:2	93	11	106	1
Bifenthrin	Pyrethroid	Insecticide	GC-MS:1	91	5	107	5
Boscalid	Anilide	Fungicide	GC-MS:2	109	21	118	13
BromocoNDzole	Azole	Fungicide	GC-MS:2	99	18	107	16
Butralin	2,6-Dinitroaniline	Herbicide	GC-MS:1	79	7	96	7
Butylate	Thiocarbamate	Herbicide	GC-MS:1	80	12	108	13
Captan	Thiophthalimide	Fungicide	GC-MS:2	77	17	83	22
Carbaryl	N-Methyl Carbamate	Insecticide	GC-MS:1	72	11	118	8
Carbendazim	Benzimidazole	Fungicide	LC-MS/MS	>130	>130	>130	>130
Carbofuran	N-Methyl Carbamate	Insecticide	GC-MS:1	70	25	112	1
Chlorantraniliprole	Anthranilic diamide	Insecticide	LC-MS/MS	81	2	94	13
Chlorothalonil	Substituted Benzene	Fungicide	GC-MS:2	58	8	71	3
Chlorpyrifos	Organophosphorus	Insecticide	GC-MS:1	80	7	94	11
Chlorpyrifos oxon	Organophosphorus	Insecticide	GC-MS:1	80	7	90	16
Clomazone	Unclassified	Herbicide	GC-MS:1	86	8	112	11
Clothianidin	Neonicotinoid	Insecticide	LC-MS/M	73	1	82	15
Coumaphos	Organophosphorus	Insecticide	GC-MS:1	92	13	104	12
Cyantraniliprole	Anthranilic diamide	Insecticide	LC-MS/MS	93	5	108	18
Cyazofamid	Azole	Fungicide	LC/MS/MS	61	3	39	8
Cycloate	Thiocarbamate	Herbicide	GC-MS:1	113	11	112	2
Cyfluthrin	Pyrethroid	Insecticide	GC-MS:1	83	9	112	18
Cyhalofop-butyl	Aryloxyphenoxy propionic acid	Herbicide	GC-MS:1	71	10	90	9
Cyhalothrin	Pyrethroid	Insecticide	GC-MS:1	71	6	90	11
Cymoxanil	Unclassified	Fungicide	LC/MS/MS	78	3	75	13
Cypermethrin	Pyrethroid	Insecticide	GC-MS:1	81	11	100	9
CyprocoNDzole	Azole	Fungicide	GC-MS:2	87	13	106	13
Cyprodinil	Pyrimidine	Fungicide	GC-MS:2	90	10	102	9
DCPA	Alkyl Phthalate	Herbicide	GC-MS:1	78	6	97	7
DCPMU	Urea	Degradate	LC/MS/MS	74	3	90	14
DCPU	Urea	Degradate	LC/MS/MS	76	2	99	13
Deltamethrin	Pyrethroid	Insecticide	GC-MS:1	71	11	89	11

Desthio-prothiocoNDzole	Unclassified	Degradate	LC/MS/MS	117	4	134	21
Desulfinylfipronil	Unclassified	Degradate	GC-MS:1	86	8	116	16
Desulfinylfipronil amide	Unclassified	Degradate	GC-MS:1	96	17	90	10
Diazinon	Organophosphorus	Insecticide	GC-MS:1	92	6	108	17
Diazoxon	Organophosphorus	Degradate	GC-MS:1	78	23	105	20
DifenocoNDzole	Azole	Fungicide	GC-MS:2	81	22	102	28
Dimethomorph	Morpholine	Fungicide	GC-MS:2	100	23	107	16
Dinotefuran	Neonicotinoid	Insecticide	LC/MS/MS	42	7	29	7
Dithiopyr	Pyridinecarboxylic acid	Herbicide	GC-MS:1	96	6	115	8
Diuron	Urea	Herbicide	LC/MS/MS	78	5	97	17
EPTC	Thiocarbamate	Herbicide	GC-MS:1	76	10	103	11
Esfenvalerate	Pyrethroid	Insecticide	GC-MS:1	71	7	91	10
Ethaboxam	Unclassified	Fungicide	LC/MS/MS	135	4	150	17
Ethalfluralin	2,6-Dinitroaniline	Herbicide	GC-MS:1	74	6	99	9
Etofenprox	Pyrethroid Ether	Insecticide	GC-MS:1	72	7	90	9
Etoxazole	Diphenyl Oxazoline	Insecticide	GC-MS:2	94	12	101	4
Famoxadone	Oxazolidinedione	Fungicide	GC-MS:2	83	24	101	28
FeNDmidone	Imidazole	Fungicide	GC-MS:2	89	11	105	12
FeNDrimol	Pyrimidine	Fungicide	GC-MS:2	98	14	106	8
FenbucoNDzole	Azole	Fungicide	GC-MS:2	97	18	111	19
Fenhexamid	Anilide	Fungicide	GC-MS:2	84	10	111	8
Fenpropathrin	Pyrethroid	Insecticide	GC-MS:1	79	6	89	4
Fenpyroximate	Pyrazole	Insecticide	GC-MS:1	ND	ND	ND	ND
Fenthion	Organophosphorus	Insecticide	GC-MS:1	83	3	88	15
Fipronil	Pyrazole	Insecticide	GC-MS:1	95	10	117	8
Fipronil sulfide	Unclassified	Degradate	GC-MS:1	96	7	114	6
Fipronil sulfone	Unclassified	Degradate	GC-MS:1	81	7	98	7
Flonicamid	Unclassified	Insecticide	LC/MS/MS	72	1	31	11
FluaziNDm	2,6-Dinitroaniline	Fungicide	GC-MS:2	102	26	117	4
Fludioxonil	Unclassified	Fungicide	GC-MS:2	88	10	110	12
FlufeNDcet	Anilide	Herbicide	GC-MS:1	83	9	114	11
Flumetralin	2,6-Dinitroaniline	Plant growth regulator	GC-MS:1	74	5	91	9
Fluopicolide	Benzamide Pyridine	Fungicide	GC-MS:2	100	14	121	6
Fluopyram	Amide	Fungicide	GC-MS:2	113	13	115	12
Flupyradifurone	Butenolides	Insecticide	LC/MS/MS	66	<1	81	14
Fluoxastrobin	Strobin	Fungicide	GC-MS:2	117	7	104	9
Fluridone	Unclassified	Herbicide	LC/MS/MS	94	7	110	17
Flusilazole	Azole	Fungicide	GC-MS:2	78	10	94	12
Flutolanil	Anilide	Fungicide	GC-MS:2	93	12	109	7
Flutriafol	Azole	Fungicide	GC-MS:2	93	11	109	11
Fluxapyroxad	Anilide, Pyrazole	Fungicide	GC-MS:2	106	16	119	9
Hexazinone	Triazinone	Herbicide	GC-MS:1	89	13	103	7
Imidacloprid	Neonicotinoid	Insecticide	LC-MS/MS	87	4	95	15
Indaziflam	Alkylazine	Herbicide	GC-MS	ND	ND	ND	ND
Indoxacarb	Unclassified	Insecticide	GC-MS:2	89	30	96	34
IpcoNDzole	Triazole	Fungicide	GC-MS:2	93	18	105	18
Iprodione	Dicarboximide	Fungicide	GC-MS:2	103	31	86	7
Isofetamid	Amide	Fungicide	GC-MS:2	99	16	113	10
Kresoxim-methyl	Strobin	Fungicide	GC-MS:2	78	11	92	10
Malaoxon	Organophosphorus	Degradate	GC-MS:2	51	20	115	23
Malathion	Organophosphorus	Insecticide	GC-MS:1	80	6	102	14
Mandipropamid	Amide	Fungicide	LC-MS/MS	95	4	112	17
Metalaxyl	Xylylalanine	Fungicide	GC-MS:2	91	10	117	16
Metaldehyde	Aldehyde	Molluscicide	LC-MS/MS	ND	ND	ND	ND

MetcoNDzole	Azole	Fungicide	GC-MS:2	88	15	106	14
Methamidophos	Organophosphorus	Insecticide	GC-/MS:1	ND	ND	ND	ND
Methidathion	Organophosphorus	Insecticide	GC-MS:1	88	12	99	7
Methoprene	Juvenile hormone mimic	Insect growth regulator	GC-MS:1	87	9	95	14
Methoxyfenozide	Diacylhydrazine	Insecticide	LC/MS/MS	80	5	100	18
Methyl parathion	Organophosphorus	Insecticide	GC-MS:1	67	9	91	22
Metolachlor	Chloroacetanilide	Herbicide	GC-MS:1	97	6	113	1
MoliNDte	Thiocarbamate	Herbicide	GC-MS:1	94	10	107	3
Myclobutanil	Azole	Fungicide	GC-MS:2	86	9	108	16
NDpropamide	Amide	Herbicide	GC-MS:1	96	7	115	6
Novaluron	Benzoylurea	Herbicide	GC-MS:2	18	4	17	3
Oryzalin	2,6-Dinitroaniline	Herbicide	LC/MS/MS	52	1	51	9
Oxadiazon	Unclassified	Herbicide	GC-MS:1	81	6	94	4
Oxyfluorfen	Diphenyl ether	Herbicide	GC-MS:1	71	7	95	8
p,p'-DDD	Organochlorine	Insecticide, breakdown product	GC-MS:1	83	5	102	8
p,p'-DDE	Organochlorine	Degradate	GC-MS:1	71	3	90	7
p,p'-DDT	Organochlorine	Insecticide	GC-MS:1	86	8	102	11
Paclobutrazol	Azole	Plant growth regulator	GC-MS:2	95	13	90	9
Pebulate	Thiocarbamate	Herbicide	GC-MS:1	92	13	115	7
Pendimethalin	2,6-Dinitroaniline	Herbicide	GC-MS:1	88	7	99	5
Pentachloroanisole	Organochlorine	Degradate	GC-MS:1	66	7	82	7
Pentachloronitrobenzene	Substituted Benzene	Fungicide	GC-MS:2	82	11	108	5
Penthiopyrad	Pyrazole	Fungicide	LC-MS/MS	60	4	71	13
Permethrin	Pyrethroid	Insecticide	GC-MS:1	81	7	92	5
Phenothrin	Pyrethroid	Insecticide	GC-MS:1	87	6	101	6
Phosmet	Organophosphorus	Insecticide	GC-MS:1	84	16	95	14
Picoxystrobin	Strobin	Fungicide	GC-MS:2	101	10	112	5
Piperonyl butoxide	Unclassified	Synergist	GC-MS:1	94	10	120	9
Prodiamine	2,6-Dinitroaniline	Herbicide	GC-MS:1	82	7	113	21
Prometon	Triazine	Herbicide	GC-MS:1	ND	ND	ND	ND
Prometryn	Triazine	Herbicide	GC-MS:1	119	14	110	6
Propanil	Anilide	Herbicide	GC-MS:1	112	9	117	12
Propargite	Unclassified	Insecticide	GC-MS:1	116	12	89	4
PropicoNDzole	Azole	Fungicide	GC-MS:2	92	15	113	14
Propyzamide	Amide	Herbicide	GC-MS:1	109	12	119	17
Pyraclostrobin	Strobin	Fungicide	GC-MS:2	74	1	69	15
Pyridaben	Unclassified	Insecticide	GC-MS:1	89	8	104	8
Pyrimethanil	Pyrimidine	Fungicide	GC-MS:2	94	10	106	4
Quinoxyfen	Quinoline	Fungicide	GC-MS:2	105	13	119	5
Resmethrin	Pyrethroid	Insecticide	GC-MS:1	84	10	98	8
Sedaxane	Anilide, Pyrazole	Fungicide	GC-MS:2	107	22	122	13
Simazine	Triazine	Herbicide	GC-MS:1	92	7	114	4
Strychnine	Alkaloid	Rodenticide	LC-MS/MS	ND	ND	ND	ND
Sulfometuron methyl	Urea	Herbicide	LC-MS/MS	ND	ND	ND	ND
tau-FluvaliNDte	Pyrethroid	Insecticide	GC-MS:1	58	6	86	15
TebucoNDzole	Azole	Fungicide	GC-MS:2	89	16	113	17
Tebupirimfos	Organophosphorus	Insecticide	GC-MS:1	84	9	92	10
Tebupirimfos oxon	Organophosphorus	Degradate	GC-MS:2	97	16	115	11
Tefluthrin	Pyrethroid	Insecticide	GC-MS:1	94	4	121	9
TetracoNDzole	Azole	Fungicide	GC-MS:2	80	10	99	11
Tetradifon	Unclassified	Insecticide	GC-MS:1	87	9	101	6
Tetramethrin	Pyrethroid	Insecticide	GC-MS:1	97	9	107	4

Thiabendazole	Benzimidazole	Fungicide	LC-MS/MS	91	11	107	13
Thiacloprid	Neonicotinoid	Insecticide	LC-MS/MS	54	3	69	11
Thiamethoxam	Neonicotinoid	Insecticide	LC-MS/MS	88	5	82	18
Thiazopyr	Pyridinecarboxylic acid	Herbicide	GC-MS:1	91	6	110	5
Thiobencarb	Thiocarbamate	Herbicide	GC-MS:1	85	8	103	3
Tolfenpyrad	Pyrazole	Insecticide	LC-MS/MS	113	12	96	14
Triadimefon	Azole	Fungicide	GC-MS:2	89	10	113	13
Triadimenol	Azole	Fungicide	GC-MS:2	97	11	88	9
Triallate	Thiocarbamate	Herbicide	GC-MS:1	92	14	116	3
Tribufos	Organophosphorus	Defoliant	GC-MS:2	95	13	106	7
Triclopyr	Pryridine	Herbicide	LC-MS/MS	11	1	ND	ND
Trifloxystrobin	Strobin	Fungicide	GC-MS:2	93	14	110	11
Triflumizole	Azole	Fungicide	GC-MS:2	84	11	104	12
Trifluralin	2,6-Dinitroaniline	Herbicide	GC-MS:1	74	7	93	7
TriticoNDzole	Azole	Fungicide	GC-MS:2	90	16	111	17
Zoxamide	Amide	Fungicide	GC-MS:2	111	28	94	28

The surrogate recoveries (**Table 5**) for the GC-MS compounds were generally acceptable, however, $^{13}C_{12}$-*p,p'*-DDE had low recovery using the HLB disk. The surrogate recoveries for the LC-MS/MS compounds, d_4-imidacloprid and monuron, were low compared to the GC-MS surrogates suggesting that the LC surrogates may have eluted off the disk during sample loading. Although the laboratory spike test did not mimic field conditions including flow and duration of deployment, low surrogate recoveries may indicate that some surrogate compounds can leach off the disks during deployment in the field.

Table 5. Surrogate recoveries for compounds analyzed GC-MS and LC-MS/MS Methods.1 and 2 denote injection).

Pesticide	Chemical class	Pesticide type	Analytical method	HLB (% Rec)	Std. Dev.	SDB-RPS (% Rec)	Std. Dev.
$^{13}C_3$-Atrazine	Triazine	Herbicide	GC-MS:1	88	9	80	15
$^{13}C_{12}$-*p,p'*-DDE	Organochlorine	Degradate	GC-MS:1	61	9	72	11
$^{13}C_4$-Fipronil	Pyrazole	Insecticide	GC-MS:1	100	22	105	10
d_4-Imidacloprid	Neonicotinoid	Insecticide	LC-MS/MS	50	12	18	11
Monuron	Urea	Herbicide	LC-MS/MS	57	19	25	12
$^{13}C_6$-*cis*-Permethrin	Pyrethroid	Insecticide	GC-MS:1	84	7	90	12
d_{14}-Trifluralin	2,6-Dinitroaniline	Herbicide	GC-MS:1	71	10	79	11

New Compound Addition

In order for the addition of compounds to be successful they must first be compatible with the instrumental methods by exhibiting good analytic response. Secondly, the compound must be extinguishable from the background noise of the sampling media or sample matrix. Lastly, the compound must be extractable by the

disk and recoverable using the elution method. The details of each compounds ability to meet these measures are shown in **Table 6**.

Table 6. Compound performances in laboratory method. ND: Not Detected; LOD: Lower Limit of Detection.

	Instrument Response	Distinguishable from Background	Method Recovery
Aminopyralid	Poor	Poor	ND
2,4-D	Adequate	Adequate	<LOD
Metaldehyde	Adequate	Poor	<LOD
Methamidophos	Adequate	Poor	ND
Strychnine	Adequate	Adequate	ND
Sulfometuron methyl	Adequate	Poor	ND
Triclopyr	Adequate	Adequate	<LOD

The compounds aminopyralid, 2,4-D, metaldehyde, methamidophos, strychnine, sulfometuron methyl, and triclopyr were added to our instrumental methods with some compounds needing instrumental method modification to be successful. The compound methamidophos and sulfometuron methyl was added to the Injection 1 program on the GC-MS and GC-MS/MS but both had poor retention resulting in an early elution times. Also, the most abundant molecular ions for the compounds were of low molecular weight which can be problematic for signal to noise ratio. The compounds were not successfully recovered from the spike tests using either disk type. Metaldehyde was added to the LC-MS/MS method. Metaldehyde only had one abundant transition and, therefore, no qualifier transition. Without a qualifier the compound was unable to be distinguished from the background with confidence when analyzing the spiked disks. Aminopyralid can be analyzed by LC-MS/MS in ESI+ mode, however, it was not fully retained by the C18 column using our 1% formic acid in water: ACN mobile phase gradient and had to be separated using water: ACN to inhibit peak splitting. Even with this modification the response of the compound was very low and the compound was not detected in the spike study. The modified mobile phase was also needed for retention of strychnine. Strychnine performed well in the instrumental method, however, it was not recovered even in low amounts in the spike test. The compounds 2,4-D and triclopyr were both analyzed in ESI- mode successfully and were recovered in very low percentages from the spiked disks. The inability for the new compounds to successfully work in the spike test could be from lack of retention in the disks during the extraction or from poor recovery during the elution from the disk. Typically grab

water samples are acidified prior to extraction when analyzing for acidic compounds in order to promote adherence to the sorption material. Then they are eluted with a basic eluent. An acidified extraction cannot be controlled for passive sampling disks. Different eluents may yield better success for some of the compounds. For instance, metaldehyde has seen acceptable recovery from the Atlantic® HLB disks using ethyl acetate as an eluent (Mills and Gravell, 2015). Aminopyralid and methamidophos' lack of acceptable recoveries in the spike tests were likely also due to poor performance in the instrumental methods, therefore, it is unknown if they are incompatible with the disk extraction or elution method.

In summary, a working method has been established for both the Atlantic® HLB and Empore™ SDB-RPS disks. The laboratory spike experiment suggests that both disks types are able to extract our target group of compounds (**Table 4**) excluding the additional compounds requested to be added to the methods (aminopyralid, 2,4-D, metaldehyde, methamidophos, strychnine, sulfometuron methyl, and triclopyr). The laboratory spike data suggested that the HLB disk has better recovery for LC-MS/MS compounds than the SDB-RPS while the SDB-RPS disk performs better for GC-MS and GC-MS/MS compounds. However, the field data suggests that overall the Empore™ SDB-RPS disk performs better in the field than the HLB disk. An additional field test was conducted at an agricultural/urban site known to have a prevalence of pesticide detections (DeParsia and others, in press) and the data will be used to confirm whether the SDB-RPS disk indeed does perform better in the field. A laboratory test will be conducted to assess potential losses of extracted pesticides during shipment and disk storage prior to elution to determine acceptable holding times for the disk media as requested by our collaborator. An additional laboratory spike test will be conducted for all compounds methods using the DLM to see if recovery is affected or if certain pesticides adhere to the DLM itself. These results will be compared to the recoveries reported herein. The results from the additional study will be part of a larger project, Sierra Passive Sampling II, which will take place in 2018.

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Table 2. Retention times, quantitation ions and confirmation ions for pesticides analyzed by LC/MS/MS. Analysis is

Compound	Retention Time (min)	Precursor Ion	Fragmentor	Quantitative Ion	Collision Energy
Thiamethoxam Degradate (CGA-353042)	0.78	116	83	86	4
Imidacloprid desnitro	4.97	211	126	126	20
Thiamethoxam Degradate (NOA-407475)	5.02	247	102	132	28
Dinotefuran	5.05	203	69	113	4
Carbendazim	5.09	192	107	160	12
Thiabendazole	5.15	202	146	175	24
Strychnine	5.21	335	180	184	40
Thiamethoxam	5.46	292	84	211	8
Imazapyr	5.45	262	87	69	24
Flonicamid	5.47	230	131	203	12
Imidacloprid urea	5.47	212	131	128	16
Clothianidin des methyl	5.51	236	93	132	8
d3-clothianidin (internal standard)	5.60	253	73	172	8
6-chloronicotinic acid	5.60	158	126	122	16
Metaldehyde	5.65	199	141	67	4
Clothianidin	5.67	250	79	169	8
Thiamethoxam Degradate (CGA-355190)	5.71	248	112	175	16
Thiamethoxam Degradate (NOA-404617)	5.72	237	84	175	8
Imidacloprid	5.77	256	89	209	12
d_4-Imidacloprid (surrogate)	5.77	260	91	213	12
Acetamiprid	5.83	223	102	126	16
Tricyclazole	5.88	190	121	136	28
Cymoxanil	6.01	199	55	128	0
Thiacloprid	6.07	253	117	126	16
Flupyradifurone	6.07	289	141	126	20
Sulfoxaflor	6.16	278	49	174	4
DCPU	6.29	205	116	127	28
Monuron (surrogate)	6.31	199	96	72	12
Ethaboxam	6.45	321	146	183	20
Mesotrione	6.47	340	160	228	12
DCPMU	6.56	219	106	127	32
Cyantraniliprole	6.73	473	126	284	8
Carboxin (Carbathiin)	6.75	236	98	143	12
Diuron	6.77	233	106	72	20
Penoxsulam	6.83	484	155	195	28
3,4-DCA	6.90	162	123	127	20
Chlorantraniliprole	7.00	492	117	284	8
Fluridone	7.08	330	170	309	36
Bicyclopyrone	7.22	400	131	324	16
Mandipropamid	7.26	412	97	328	8
Desthio-prothioconazole	7.30	312	146	70	24
Oxathiapiprolin	7.37	540	150	500	24
Methoxyfenozide	7.43	369	92	149	12
Oryzalin	7.50	347	132	288	12
Tebufenozide	7.63	353	74	133	12
Penthiopyrad	7.70	360	102	276	8
Cyazofamid	7.71	325	88	108	8
Tolfenpyrad	8.24	384	175	197	24
2,4-D	0.75	219	88	161	4
Triclopyr	0.77	254	83	218	0

done in dynamic MRM mode.

Confirmation Ion	Collison Energy	ESI mode
57	16	Positive
90	36	Positive
161	12	Positive
87	8	Positive
105	40	Positive
131	32	Positive
156	50	Positive
181	20	Positive
41	48	Positive
174	16	Positive
99	16	Positive
		Positive
113	28	Positive
78	28	Positive
		Positive
132	12	Positive
56	44	Positive
147	20	Positive
89	12	Positive
179	16	Positive
56	12	Positive
163	20	Positive
111	12	Positive
90	40	Positive
90	48	Positive
154	24	Positive
162	12	Positive
126	24	Positive
200	24	Positive
104	32	Positive
162	12	Positive
442	12	Positive
87	20	Positive
160	24	Positive
164	36	Positive
109	32	Positive
451	12	Positive
259	50	Positive
228	40	Positive
125	36	Positive
125	36	Positive
163	50	Positive
313	0	Positive
243	12	Positive
203	0	Positive
256	16	Positive
44.1	28	Positive
145	28	Positive
125	24	Negative
196	4	Negative

QUALITY ASSURANCE PROJECT PLAN

COORDINATED PESTICIDE RECONNAISSANCE STUDY

January 1, 2015 – June 30, 2017

Prepared by

U.S. Geological Survey

Draft v. 1.0

Prepared for the:
State Water Resources Control Board

SECTION A1. TITLE AND APPROVAL SHEETS; CITATION FOR QAPP; PREFACE

Program Title	**Coordinated Pesticide Recognizance Study**
Performing Laboratory	U.S. Geological Survey Organic Chemistry Research Laboratory (OCRL)
Primary Contact	James Orlando, Hydrologist, (916) 278-3271
Effective Date	This Quality Assurance Project Plan (QAPP) is effective from January 1, 2015 to June 30, 2017 unless otherwise revised, approved and distributed accordingly at an earlier date.
Citation for QAPP	U.S. Geological Survey, 2014, Quality Assurance Project Plan for the Central Valley Regional Water Quality Control Board. 87 pages.

Preface

This Quality Assurance Project Plan (QAPP) document defines procedures and criteria that will be used for projects conducted by the U.S. Geological Survey Organic Chemistry Research Laboratory (OCRL) in association with the Central Valley Regional Water Quality Control Board (CVRWQCB). Included are criteria for data acceptability, procedures for sampling, testing (including deviations) and calibration, as well as preventative and corrective measures. The responsibilities of USGS OCRL and of the CVRWQCB Contractors are also contained within.

The CVRWQCB in coordination with USGS OCRL personnel are responsible for providing a project description that includes a project overview and its goals as well as for submitting a field site list and rationale, sampling frequency, and types and numbers of analyses to be conducted.

This QA project plan has been drafted and approved by the OCRL prior to the performance of any analyses. If, after fully reading this document and becoming knowledgeable of potential deviations, constraints and considerations that must be taken into account, the CVRWQCB wishes to proceed with testing by USGS OCRL, this QAPP will be applied.

APPROVALS:

U.S. Geological Survey

_____ _____
James L. Orlando, Hydrologist — Date
USGS Principal Investigator

_____ _____
Michelle Hladik, Research Chemist — Date
USGS Co-Principal Investigator

_____ _____
Megan McWayne, Chemist — Date
USGS Laboratory Manager

_____ _____
Lisa Olsen, Water Quality Specialist — Date
USGS Quality Assurance/Quality Control Officer

California Regional Water Quality Control Board

_____ _____
Melissa Dekar — Date
Contract Manager
Regional Water Quality Control Board – Region 5

_____ _____
Robert LaCasse — Date
Contract Analyst
State Water Resources Control Board

_____ _____
Renee Spears — Date
SWRCB Quality Assurance/Quality Control Officer

SECTION A2. TABLE OF CONTENTS

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SECTION A3. DISTRIBUTION LIST AND CONTACT INFORMATION

A copy of this QAPP, in hardcopy or electronic format, is to be received and retained by at least one person from each participating entity. At least one person from each entity (names shown with asterisk*) shall be responsible for receiving, retaining and distributing the QAPP to their participating staff within their own organization. Contact information for the primary contact person for each participating organization is also provided in Table 1.

Table 1. Contact Information

Name	Agency, Company or Organization
U.S. Geological Survey	
James Orlando*, Michelle Hladik, Megan McWayne, Lisa Olsen	USGS California Water Science Center 6000 J St Placer Hall Sacramento CA 95819 Phone: 916-278-3000 Email: jorlando@usgs.gov
State Water Resources Control Board	
SWRCB Contract Analyst Robert LaCasse	SWRCB 1001 I Street, 18th Floor, 18-54C Sacramento, CA 95814 Phone: 916- 341-5929 Email: robert.lacasse@waterboards.ca.gov
Central Valley Regional Water Quality Control Board	
CVRWQCB Project Director/Contract Manager Melissa Dekar	CVRWQCB 11020 Sun Center Drive #200 Rancho Cordova, CA 95670 Phone: 916-464-4603 Email: melissa.dekar@waterboards.ca.gov

SECTION A4. PROGRAM/TASK ORGANIZATION

The OCRL is managed by personnel of the Pesticide Fate Research Group (PFRG) within the U.S. Geological Survey California Water Science Center (CAWSC) and is located in Sacramento California. One focus of the OCRL is on developing new analytical methods for measuring the concentrations of new and understudied pesticides in the environment. In addition to this method development work the OCRL has a number of fully developed and documented analytical methods which are available for routine analysis of water, sediment, and tissue samples and that offer an extensive list of pesticide analytes. PFRG personnel work closely with Federal, State and local cooperators within California and throughout the United States on a wide array of pesticide occurrence, fate and transport studies and have been active within the CAWSC since the late 1980's. OCRL personnel and responsibilities associated with the cooperative study which is the focus of this QAPP document are outlined in Table 2.

4.1 Involved parties and roles

Robert LaCasse (SWRCB) will serve as the Contract Analyst. The Contract Analyst will 1) provide all technical and administrative services as needed for contract completion, 2) monitor, supervise and review all work performed, and 3) coordinate budgeting and scheduling to assure that the contract is completed within budget, on schedule and in accordance with approved procedures, applicable laws and regulations.

Melissa Dekar (CVRWQCB) will serve as the Project Director (PD) and Contract Manager. The PD will 1) review and approve the QAPP, 2) review, evaluate and document project reports, 3) coordinate with other monitoring efforts in the study area, and 4) verify completeness of all tasks.

James Orlando (USGS) will serve as the Principal Investigator (PI). The PI will 1) review and approve the QAPP, 2) provide oversight on study design and development, 3) provide project updates to the PD, and 4) provide the contracting entity with a final report upon completion of this project.

Michelle Hladik (USGS) will serve as the Co-Principal Investigator and Laboratory Manager (CoPI) and will provide oversight for all sample processing and analysis done by USGS OCRL. Specific duties for the CoPI are to 1) review and approve the QAPP, 2) provide pricing for all lab work to be done, 3) authorize and approve the purchase of all supplies related to the project, and 4) conduct pesticide analyses.

Megan McWayne (USGS) will serve as the Laboratory Manager (LM) and will provide oversight for all sample processing done by USGS OCRL. Specific duties for the LM are to 1) review and approve the QAPP, 2) purchase supplies related to the project, 3) oversee laboratory safety, and 4) ensure that all laboratory activities are completed within the proper timelines.

Corey Sanders (USGS) will serve as a co-data manager/reporter. Specific duties include 1) reviewing, managing, and reporting the data generated by the project.

4.2 Quality Assurance Officer role

Lisa Olsen is the USGS CAWSC Quality Assurance Officer (QAO). The QAO's role is to ensure that quality control for sample processing and data analysis procedures described in this QAPP are maintained throughout the project.

The QAO will review and assess all procedures during the life of the contract against QAPP requirements and assess whether the procedures are performed according to protocol. She will report all findings to the PI, including all requests for protocol amendments.

4.3 Persons responsible for QAPP update and maintenance

Revisions and updates to this QAPP will be carried out by the PI, in consultation with the CoPI, LM, and QAO. All changes will be considered draft until reviewed by the PD.

4.3.1 QAPP distribution

Copies of this QAPP will be distributed to all parties involved in the project. Any future amended QAPPs will be held and distributed in the same fashion. All originals of these first and subsequent QAPPs will be held on site at USGS CAWSC.

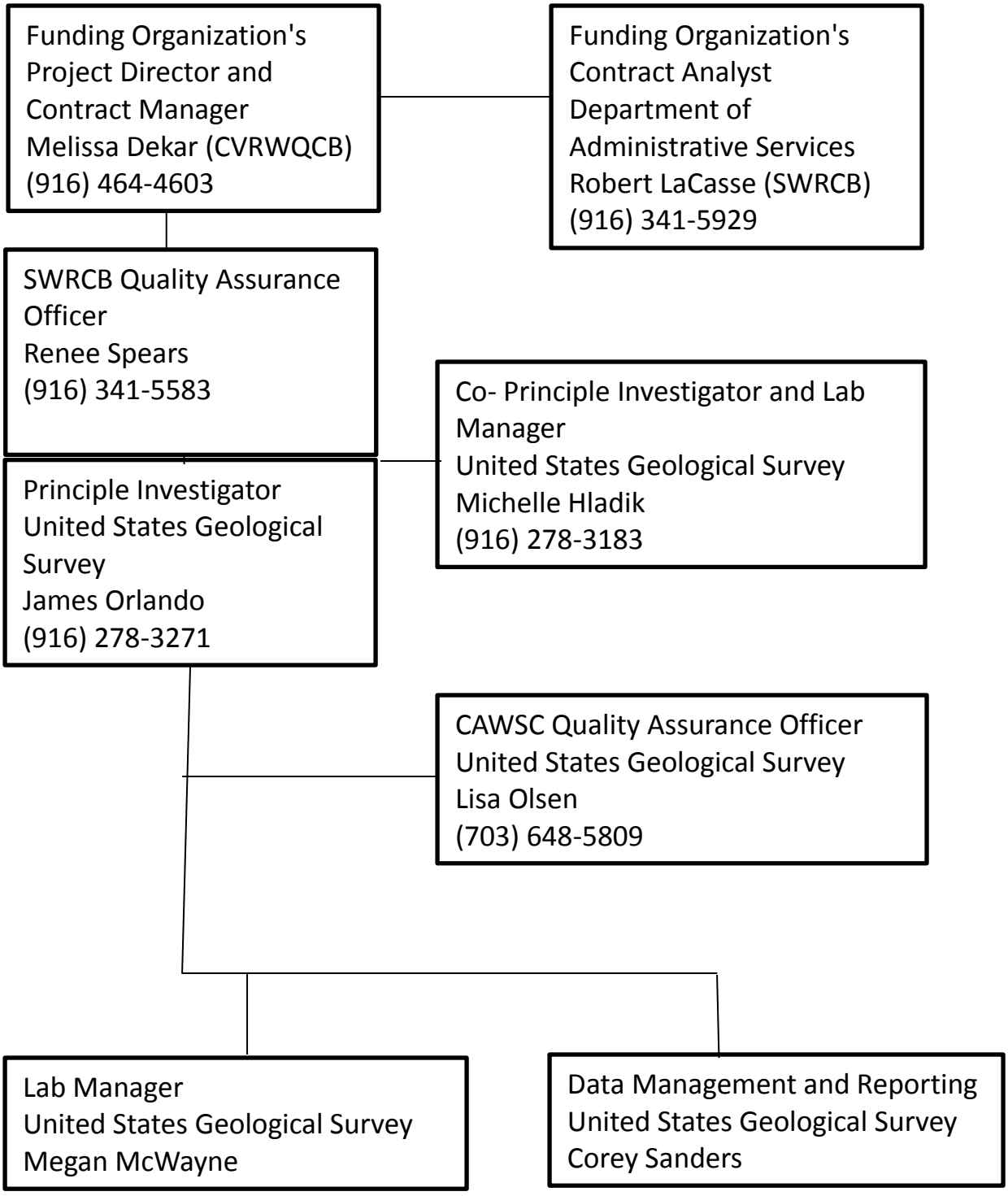


Figure 1 Project Organizational Chart

Table 2 Project responsibilities

Responsibilities		
Sampling	Sampling Design	James Orlando; USGS
		Melissa Dekar; CVRWQCB
	Sample collection, calibration of field instruments, field analysis	Various State agency field crews
	Sample Delivery	
	Sample custody/storage and lab instrument calibration	Megan McWayne; USGS
Pesticide Analysis	Water & Sediment: insecticides, herbicides, fungicides	Michelle Hladik; USGS
	Quality Control and Data Validation	Michelle Hladik, James Orlando; USGS
Project Direction	James Orlando; USGS Melissa Dekar; CVRWQCB	
Contract Management	Melissa Dekar; CVRWQCB	
Data Management and Reporting	Corey Sanders; James Orlando; USGS	

SECTION A5. PROBLEM DEFINITION/BACKGROUND

5.1 Problem statement

Pesticides are used to control pests in both urban and agricultural settings throughout the State of California. Many pesticides are routinely detected in surface water and in some cases have resulted in water quality impairments and impacts to beneficial uses. Each year, new pesticides are introduced into the market. Because of the way monitoring programs are typically developed and the lag time in the development of analytical methods and toxicity values for new pesticides, it can take several years or longer to identify if a new pesticide is present and/or emerging as a concern in surface waters. This project is intended to investigate the presence of new and/or understudied pesticides in surface water, particularly herbicide degradates, fungicides, and neonicotinoid insecticides for which there is limited monitoring data. The contract deliverables will be used to determine which pesticides are detected in surface water and if any are present above known toxicity values, to prioritize which pesticides, if any, warrant further investigation, and to evaluate models and monitoring protocols.

5.2 Decisions or outcomes

This study will provide data on the occurrence of a suite of 135 current-use pesticides and pesticide degradates in surface waters and 125 pesticides and degradates in associated suspend sediment, from 12 sites within California (Error! Reference source not found.**,**

Table 3).

5.3 Water quality or regulatory criteria

The results of the study will be used to determine which pesticides are detected in surface water and if any are present above known toxicity values (see Appendix A for U.S. EPA benchmark values), to prioritize which pesticides, if any, warrant further investigation, and to evaluate models and monitoring protocols.

SECTION A6. PROJECT DESCRIPTION

6.1 Work statement and produced products

This project will involve the use of two laboratory analytical methods in assessing the occurrence of 135 current-use pesticides and degradates in surface water samples and 125 pesticides and degradates in suspended sediments collected at 6 urban and 6 agriculturally dominated sites within California (

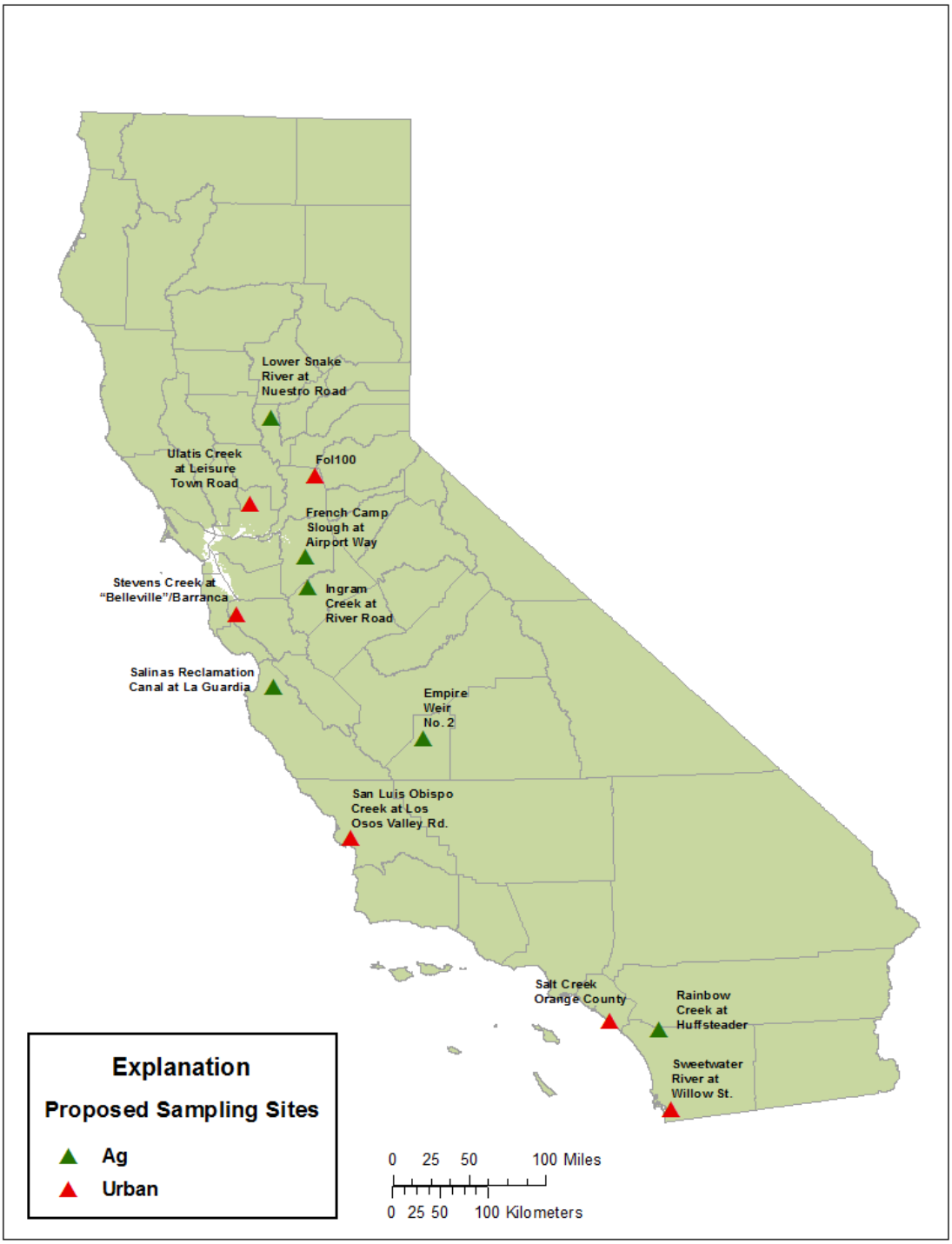
Table 3 Study Sites

Site Type	Site Name	Lat	Long	2015 Sampling Events[1]			2016 Sampling Events[2]			Coordinating Entity
				1	2	3	1	2	3	
Ag-1	309ALG – Salinas Reclamation Canal at La Guardia	36.65683	-121.6135	Wet	Wet	Dry	Wet	Wet	Dry	Region 3 Ag Order (Mary Hamilton)
Ag-2	French Camp Slough @ Airport Way	37.88172	-121.24933	Wet	Wet	Dry	Wet	Wet	Dry	Region 5 Delta Ag Coalition (Susan Fregien)
Ag-3	Ingram Creek @ River Road	37.600278	-121.224167	Wet	Wet	Dry	Wet	Wet	Dry	Region 5 Westside Coalition (Susan Fregien)
Ag-4	Lower Snake River at Nuestro Road	39.1853	-121.704	Wet	Wet	Dry	Wet	Wet	Dry	Region 5 Sacramento Valley Coalition (Susan Fregien)
Ag-5	Empire Weir No. 2 (OR Stone Corral)	36.179019	-119.834037	Wet	Wet	Dry	Wet	Wet	Dry	Region 5 staff (Dave Sholes)
Ag-6	Rainbow Creek @ Huffsteader	33.415440	-117.151990	Wet	Wet	Dry	Wet	Wet	Dry	Region 9 (Helen Yu)
Urban-1	205STE060 - Stevens Creek at "Belleville"/Barranca	37.33503	-122.06384	Dry	Dry	Wet	Dry	Dry	Wet	Region 2 (Kevin Lunde)
Urban-2	310SLV - San Luis Obispo Creek at Los Osos Valley Rd.	35.24312398	-120.680152	Dry	Dry	Wet	Dry	Dry	Wet	Region 3 (Mary Hamilton)
Urban-3	Fol100	38.64559	-121.14442	Dry	Dry	Wet	Dry	Dry	Wet	Jim Orlando
Urban-4	Pleasant Grove Creek (PGC040)	38.649253	-121.144276	Dry	Dry	Wet	Dry	Dry	Wet	Department of Pesticide Regulation (Mike Ensminger)
Urban-5	SC5 - Salt Creek – Orange County	33.505573	-117.708639	Dry	Dry	Wet	Dry	Dry	Wet	UCD (Brian Anderson, Bryn Phillips

Urban-6	Sweetwater River at Willow St.	32.6581	-117.0434	Dry	Dry	Wet	Dry	Dry	Wet	Region 9 (Helen Yu)

[1,2] Dates are TBD as they are weather-dependent.

Figure 2 Map of study sites



During the study, USGS will provide brief semi-annual reports to the CVRWQCB PD which will include a summary of completed activities and data results in tabular form summarizing chemical analyses of project samples completed during the previous quarter (subject to approval and release of the data by the USGS PI and QAO).

Upon completion of the project USGS will provide a peer reviewed data report describing in detail the project design, analytical methods used and results of all pesticide analyses.

6.2 Constituents to be monitored and measurement techniques

This study will employ two documented laboratory analytical methods for the analysis of pesticides in water and suspended sediment. The first method analyzes for 125 pesticides and pesticide degradates in filtered water and suspended sediment by gas chromatography with mass spectrometry (GC/MS) following procedures described by Hladik and others (2008, 2009). The second analytical method uses liquid chromatography with tandem mass spectrometry (LC/MS/MS) as described in Hladik and Calhoun (2012) to analyze for 10 pesticides and pesticide degradates in filtered water. Pesticides to be analyzed during this project are shown in

Table 4 List of pesticide analytes

GC/MS

Compound	Type	Class	Water MDL (ng/L)
3,4-DCA	Degradate	Urea	8.3
3,5-DCA	Degradate	Aniline	7.6
Acibenzolar-S-methyl	Fungicide	Benzothiadiazole	3.0
Alachlor	Herbicide	Chloroacetanilide	1.7
Allethrin	Insecticide	Pyrethroid	6.0
Atrazine	Herbicide	Triazine	2.3
Azoxystrobin	Fungicide	Strobilurin	3.1
Benefin (Benfluralin)	Herbicide	Dinitroaniline	2.0
Bifenthrin	Insecticide	Pyrethroid	4.7
Boscalid	Fungicide	Pyridine	2.8
Butralin	Herbicide	Dinitroaniline	2.6
Butylate	Herbicide	Thiocarbamate	1.8
Captan	Fungicide	Phthalimide	10.2
Carbaryl	Insecticide	Carbamate	6.5
Carbofuran	Insecticide	Carbamate	3.1
Chlorothalonil	Fungicide	Chloronitrile	4.1
Chlorpyrifos	Insecticide	Organophosphate	2.1
Chlorpyrifos OA	Degradate	Organophosphate	5.0
Clomazone	Herbicide	Isoxazlidinone	2.5
Coumaphos	Insecticide	Organophosphate	3.1
Cycloate	Herbicide	Thiocarbamate	1.1
Cyfluthrin	Insecticide	Pyrethroid	5.2
Cyhalofop-butyl	Herbicide	Aryloxyphenoxypropionate	1.9
Cyhalothrin	Insecticide	Pyrethroid	2.0
Cypermethrin	Insecticide	Pyrethroid	5.6
Cyproconazole	Fungicide	Triazole	4.7
Cyprodinil	Fungicide	Pyrimidine	7.4
DCPA	Herbicide	Benzenedicarboxylic acid	2.0
Deltamethrin	Insecticide	Pyrethroid	3.5
Diazinon	Insecticide	Organophosphate	0.9
Diazinon OA	Degradate	Organophosphate	5.0
Difenoconazole	Fungicide	Triazole	10.5
Dimethomorph	Fungicide	Morpholine	6.0
Dithiopyr	Herbicide	Pyridine	1.6
EPTC	Herbicide	Thiocarbamate	1.5
Esfenvalerate	Insecticide	Pyrethroid	3.9
Ethalfluralin	Herbicide	Aniline	3.0
Etofenprox	Insecticide	Pyrethroid	2.2
Famoxadone	Fungicide	Oxazole	2.5
Fenamidone	Fungicide	Imidazole	5.1
Fenarimol	Fungicide	Pyrimidine	6.5
Fenbuconazole	Fungicide	Triazole	5.2
Fenhexamide	Fungicide	Anilide	7.6
Fenpropathrin	Insecticide	Pyrethroid	4.1

Fenpyroximate	Insecticide	Pyrazole	5.2
Fenthion	Insecticide	Organophosphate	5.5
Fipronil	Insecticide	Phenylpyrazole	2.9
Fipronil desulfinyl	Degradate	Phenylpyrazole	1.6
Fipronil desulfinyl amide	Degradate	Phenylpyrazole	3.2
Fipronil sulfide	Degradate	Phenylpyrazole	1.8
Fipronil sulfone	Degradate	Phenylpyrazole	3.5
Fluazinam	Fungicide	Pyridine	4.4
Fludioxinil	Fungicide	Pyrrole	7.3
Flufenacet	Herbicide	Anilide	4.7
Flumethralin	PGR	Dinitroaniline	5.8
Fluopicolide	Fungicide	Pyrimidine	3.9
Fluoxastrobin	Fungicide	Strobilurin	9.5
Flusilazole	Fungicide	Triazole	4.5
Flutolanil	Fungicide	Anilide	4.4
Flutriafol	Fungicide	Triazole	4.2
Fluxapyroxad	Fungicide	Anilide	4.8
Hexazinone	Herbicide	Triazone	8.4
Imazalil	Fungicide	Triazole	10.5
Indoxacarb	Insecticide	Oxadiazine	4.9
Iprodione	Fungicide	Dicarboxamide	4.4
Kresoxim-methyl	Fungicide	Strobilurin	4.0
Malathion	Insecticide	Organophosphate	3.7
Malathion OA	Degradate	Organophosphate	5.0
Metalaxyl	Fungicide	Phenylamide	5.1
Metconazole	Fungicide	Azole	5.2
Methidathion	Insecticide	Organophosphate	7.2
Methoprene	Insecticide	Terpene	6.4
Methylparathion	Insecticide	Organophosphate	3.4
Metolachlor	Herbicide	Chloroacetanilide	1.5
Molinate	Herbicide	Thiocarbamate	3.2
Myclobutanil	Fungicide	Triazole	6.0
Napropamide	Herbicide	Amide	8.2
Novaluron	Herbicide	Benzoylurea	2.9
Oxadiazon	Herbicide	Oxadiazolone	2.1
Oxyfluorfen	Herbicide	Nitrophenyl ether	3.1
p,p'-DDD	Degradate	Organochlorine	4.1
p,p'-DDE	Degradate	Organochlorine	3.6
p,p'-DDT	Insecticide	Organochlorine	4.0
Paclobutrazol	Fungicide	Triazole	6.2
Pebulate	Herbicide	Thiocarbamate	2.3
Pendimethalin	Herbicide	Aniline	2.3
Pentachloroanisole (PCA)	Insecticide	Organochlorine	4.7
Pentachloronitrobenzene (PCNB)	Fungicide	Organochlorine	3.1
Permethrin	Insecticide	Pyrethroid	3.4
Phenothrin	Insecticide	Pyrethroid	5.1
Phosmet	Insecticide	Organophosphate	4.4
Picoxystrobin	Fungicide	Strobilurin	4.2

Piperonyl butoxide	Synergist	Unclassified	2.3
Prodiamine	Herbicide	Dinitroaniline	5.2
Prometon	Herbicide	Triazine	2.5
Prometryn	Herbicide	Triazine	1.8
Propanil	Herbicide	Anilide	10.1
Propargite	Insecticide	Sulfite ester	6.1
Propiconazole	Fungicide	Azole	5.0
Propyzamide	Herbicide	Benzamide	5.0
Pyraclostrobin	Fungicide	Strobilurin	2.9
Pyridaben	Insecticide	Pyridazinone	5.4
Pyrimethanil	Fungicide	Pyrmidine	4.1
Quinoxyfen	Fungicide	Quinoline	3.3
Resmethrin	Insecticide	Pyrethroid	5.7
Simazine	Herbicide	Triazine	5.0
Tebuconazole	Fungicide	Azole	3.7
Tebupirimfos	Insecticide	Organophosphate	1.9
Tebupirimfos OA	Degradate	Organophosphate	2.8
Tefluthrin	Insecticide	Pyrethroid	4.2
Tetraconazole	Fungicide	Azole	5.6
Tetradifon	Insecticide	Bridged diphenyl	3.8
Tetramethrin	Insecticide	Pyrethroid	2.9
t-Fluvalinate	Insecticide	Pyrethroid	5.3
Thiazopyr	Herbicide	Pyridine	4.1
Thiobencarb	Herbicide	Thiocarbamate	1.9
Triadimefon	Fungicide	Triazole	8.9
Triadimenol	Fungicide	Triazole	8.0
Triallate	Herbicide	Carbamate	2.4
Tribufos	Herbicide	Organophosphate	3.1
Trifloxystrobin	Fungicide	Strobilurin	4.7
Triflumizole	Fungicide	Azole	6.1
Trifluralin	Herbicide	Aniline	2.1
Triticonazole	Fungicide	Azole	6.9
Zoxamide	Fungicide	Benzamide	3.5

LC-MS/MS

Compound	**Type**	**Class**	**Water MDL (ng/L)**
Acetamiprid	Insecticide	Neonicotinoid	3.6
Clothianidin	Insecticide	Neonicotinoid	6.2
Dinotefurn	Insecticide	Neonicotinoid	5.5
Imidacloprid	Insecticide	Neonicotinoid	4.9
Thiacloprid	Insecticide	Neonicotinoid	3.8
Thiamethoxam	Insecticide	Neonicotinoid	3.9
3,4-DCA (diuron degradate)	Degradate	Urea	5.2
DCPU (diuron degradate)	Degradate	Urea	4.3
DCPMU (diuron degradate)	Degradate	Urea	3.0
Diuron	Herbicide	Urea	3.2

PGR = Plant Growth Regulator

6.3 Project schedule

Table 5 Schedule of completion dates

Activity	Completion Date
Quality Assurance Plans	
- QA Plan	January 1, 2015
- Monitoring Plan	January 1, 2015
Project Management and Administration	Ongoing
Sample Collection	January 1, 2015 – December 31, 2016
Sample Analyses	
- Pesticides	January 1, 2015 –January 15, 2017
Verification and Validation of Data	
- Final Quality Inspection of Data	January 31, 2017
Data Reporting	
-Data updated to USGS NWIS database	March 1, 2016 and
-Data to CVRWQCB for upload to CEDEN	March 1, 2017
Invoicing	Ongoing
Reports	
- Progress Reports	June 30, 2015; then semi-annually
- Draft Project Report	January 1, 2017
- Draft Project Report Review by CVRWQCB	March 1, 2017
- Final Project Report	June 30, 2017

6.4 Geographical setting

Samples will be collected at 6 urban dominated and 6 agriculture dominated surface water sites located in various regions of California including the Sacramento and San Joaquin Valleys, Central Coast, and Southern California (Error! Reference source not found.**,**

Table 3).

6.5 Considerations and constraints

Pertaining to pesticide analyses, SWAMP requires sample storage at < 6° C and a holding time not to exceed 7 days for the interval between sample collection and extraction of the sample for later pesticide analysis. USGS OCRL standard operating procedures (SOP) specify sample storage at < 4° C and a holding time not to exceed 48 hours. Samples collected during this project will adhere to the OCRL SOPs for field sample collection and laboratory analyses (Appendices B, C, D, E, F, G, and H). Degradation and/or adsorption of pesticides onto container surfaces during the holding period also can result in an underestimation of concentrations. OCRL SOPs specify procedures to be followed in the laboratory during sample processing and extraction which are designed to limit bias due to adsorption. Any deviations from the above outlined procedures will be reported to the PI and PD and documented in the final report.

SECTION A7. DATA QUALITY OBJECTIVES AND ACCEPTABILITY CRITERIA FOR MEASUREMENT DATA

The purpose of the study (see sections 5.1 and 5.3) is to complete a reconnaissance investigation to assess the occurrence (frequency of detection and concentrations) of a suite of understudied pesticides (Table 4) in surface water and suspended sediment from both urban and agriculturally influenced sites within California. Regional Board staff will use the data generated to determine if particular pesticides warrant further investigation at the regional or local scale. Additionally, the data may be used to evaluate models and current monitoring programs. To ensure a robust dataset, 90% completeness is required. Strict adherence to SWAMP collection techniques, and OCRL holding times, and analytical methodology will ensure high quality data as defined by the data quality objectives (DQOs) listed in Table 6. The data will be available through several web-based data bases (e.g., CEDEN and NWIS). Users should reference the QAPP to determine whether the study data are appropriate for their intended purpose(s).

SECTION A8. SPECIAL TRAINING REQUIREMENTS/SAFETY

8.1 Specialized training and safety requirements

Laboratory technicians are trained to conduct a wide variety of activities using standard protocols to ensure samples are analyzed in a consistent manner. All new laboratory personnel attend an initial training and laboratory safety session, and thereafter attend a tri-annual general safety review. Records of these trainings are retained by the CAWSC laboratory safety officer.

8.2 Training, safety and certification documentation

Staff and safety training is documented and filed on-site at the CAWSC. Documentation consists of a record of the training data, instructor and signatures of completion. The

USGS OCRL has an annual safety inspection by USGS personnel from outside the CAWSC and is also subject to periodic OSHA safety inspections. Results, recommendations and corrective actions relative to these inspections are documented by the USGS CASWC safety specialist and laboratory safety officer.

8.3 Training staff

As employees of the federal government OCRL personnel receive annual mandated training on a variety of topics from both instructor-led and online sources. Additional laboratory specific training may be provided to OCRL personnel through commercial vendors and this training is documented within the CASWSC.

SECTION A9. DOCUMENTATION AND RECORDS

USGS staff will keep sample-collection forms, copies of chain of custody forms, and quality control sample records for each sampling event. Sample-collection forms will be kept in a bound notebook. Information recorded will include: sample identification code, collection point location, date and time of collection, names of individuals collecting samples, methods used for sample collection, and field observations. Quality-control records will document the preparation and use of quality-control samples, and equipment calibration. Chain of custody forms will have the sample identification codes, collection dates, times and locations, and signatures of all individuals in custody of the samples.

Laboratory personnel will record information for samples analyzed including: names of individuals analyzing samples, time and date of analysis, and any deviations from standard operating procedures. OCRL staff will transfer data (including metadata) from field and laboratory forms to a computerized database. The database will be utilized for data validation, assessment, and report writing. Database maintenance and documentation/records storage will be the responsibility of the PI or designee. Upon review and approval of all analytical data by the PI and QAO these data will be entered into the USGS NWIS database system where they will be publicly available in perpetuity. These same data, in SWAMP compatible format, will be transferred to the PD for upload to the SWAMP CEDEN database upon completion of the project.

SECTION B1. SAMPLING PROCESS DESIGN (EXPERIMENTAL DESIGN)

Surface water samples will be collected from 12 sites located in various areas of California (**Error! Reference source not found.**), including the Central Valley, Central Coast, and Southern California region. Sampling sites were chosen to be representative of either urban or agricultural land use (6 sites each). Initially, several state agencies/programs that conduct water quality monitoring were contacted (Department of Pesticide Regulation, Surface Water Ambient Monitoring Program, and various State Water Resources Control Board regional offices) and asked to provide lists of sampling sites that will be monitored for pesticides and toxicity in 2015 and 2016. These lists were

then complied and the final list of 12 sites was selected based on the following criteria: amount of urban or agricultural land use within the upstream watershed, historical data which indicated pesticide toxicity at the site, 303(d) or other regulatory listings for the water body, and recent pesticide use data. Sampling sites were chosen by the PI and PD in consultation with personnel from the agencies mentioned above.

At each sampling location three grab samples will be collected per year for a period of two calendar years beginning in January 2015. In general for the agricultural sites, two samples will be collected during the late winter and spring (when herbicide and fungicide use are typically greatest) and will be considered wet season events, and one sample will be collected in the summer during the dry season (when insecticide use is typically greatest). The urban sites will be sampled once during the wet season and twice during the dry season. Exact sample timing will be at the discretion of the cooperating state entity and coincide with the collection of samples for toxicity testing where possible.

SECTION B2. SAMPLING METHODS

2.1 Sample collection

In coordination with the PD and PI, samples will be collected by personnel from various State entities in concert with ongoing sampling programs managed by those entities. All samples will be collected in accordance with mandated SWAMP procedures and guidelines. Number, type and timing of field collected QA/QC samples will be determined by the USGS OCRL (Table 6) and will exceed SWAMP guidelines (Appendix J, http://www.waterboards.ca.gov/water_issues/programs/swamp/docs/mqo/6_syn_water.pdf). Project plan DQOs specify that field collected QA/QC samples will be collected at a minimum frequency of 1 per every 20 samples. Sample collection will be coordinated with several entities and each coordinating entity will be required to collect at least one field QA/QC sample during the course of the study. Sample collection is weather-dependent (wet and dry samples are required at each site); therefore, the exact timing of samples will be determined over the course of the study and in coordination with the entity responsible for sample collection.

In general, sampling containers will be rinsed three times with site water prior to filling, and containers will be filled completely, leaving no headspace to minimize volatilization. After collection, sample containers will be placed in ice chests with wet ice to maintain sample transport criteria. Samples will be shipped overnight to the USGS OCRL in Sacramento, California.

2.1.1 Sample containers

Sample containers will be provided to sampling personnel by the OCRL and will consist of certified, pre-cleaned and baked, 1 L amber glass bottles with Teflon caps.

SECTION B3. SAMPLE HANDLING AND CUSTODY PROCEDURES

Grab samples will be collected by various field crews following SWAMP protocols.

Sample containers will be labeled with the location, date, and time collected and packed in ice chests with sufficient blue or wet ice to maintain sample transport criteria. Field forms (Appendix B) provided by OCRL and chain of custody forms (COC, Appendix I) provided by the collecting entity will be filled out at the time of collection and will include site ID, site description, collection date/time, container type, sample preservation, field water chemistry measurements, sampler(s) name and requested analyses. All forms will be included with the appropriate samples during shipping. After collection, samples will be shipped overnight to the OCRL in Sacramento, CA. In general samples will only be accepted at the OCRL Monday-Friday. Field crews will need to contact the PI or PD if other arrangements are necessary. If upon arrival at the OCRL samples are found to be warm (ice melted) or if sample containers are broken the PD and PI will be immediately notified.

Water samples will generally be processed to extraction upon arrival at the OCRL. If this is not possible the samples will be refrigerated at 4°C in the dark for a period not to exceed the OCRL holding time requirement of 48 hours between sample collection and extraction. Upon arrival of samples, appropriate laboratory processing forms noting unique laboratory ID, site name, collection time and date, receiving technician's name, requested analysis, and date and time of receipt will be filled out. Signed copies of COCs will be maintained with the appropriate OCRL field and laboratory forms.

SECTION B4. ANALYTICAL METHODS

4.1 Chemical analyses

Prior to analyses all water samples will be filtered through 0.7-micrometer (μm) glass-fiber filters (Grade GF/F, Whatman, Piscataway, New Jersey) into pre-cleaned glass bottles to remove suspended material. After filtering, the pre-weighed filter papers and captured suspended sediment will be allowed to air dry in a fume hood, placed in aluminum foil, sealed in ziplock bags and then stored frozen at -20°C, for a period not to exceed 30 days following collection, until extraction and analysis.

4.1.1. Water by GC/MS

GC/MS analysis methods are based on those previously described by Hladik and others (2008, 2009). To summarize these methods, each 1-L filtered-water sample will be spiked with $^{13}C_3$-atrazine and Di-N-propyl-d_{14} trifluralin(Cambridge Isotopes, Andover, Massachusetts) as recovery surrogates. The sample is then pumped under vacuum at a flow rate of 10 milliliters per minute (mL/min) through an Oasis HLB solid-phase

extraction (SPE) cartridge (6 milliliters [mL], 500 milligrams [mg], 60 µm, Waters Corporation, Milford, Massachusetts) that has been cleaned with two column-volumes of ethyl acetate followed by two column-volumes of methanol and two column-volumes of organic-free deionized water. After extraction, approximately 1 gram (g) of sodium sulfate (Na2SO4) is added to the sample bottle to remove any residual water, and the bottles are rinsed three times with approximately 2 mL of dichloromethane (DCM) into a collection tube. The bottle rinses are concentrated to 1 mL under a gentle stream of nitrogen gas. Each cartridge is dried on a manifold by passing carbon dioxide through the cartridge for approximately 1 hour or until the SPE sorbent is dry. Each cartridge is then eluted with 12 mL of ethyl acetate, and the eluate is combined with its corresponding bottle rinse. The combined solution is then reduced under a gentle stream of dry nitrogen to a final volume of 200 microliters (µL) for analysis. An internal standard (20 µL of 2 nanograms per liter [ng/L]) containing the deuterated polycyclic aromatic hydrocarbon compounds acenaphthene-d_{10}, phenanthrene-d_{10} and pyrene-d_{10} are then added to each sample. The sample extracts are then stored (not to exceed 30 days) in a freezer at –20 °C until instrumental analysis.

Water extracts will be analyzed for 125 current-use pesticides on an Agilent 7890A GC chromatograph with an Agilent 5975C Inert XL EI mass-selective detector (MSD) system using a DB-5MS analytical column (30 meter [m]×0.25 millimeter [mm]×0.25 µm, Agilent, Palo Alto, Calif.) for separation and helium as the carrier gas. Data is collected in the selected-ion-monitoring mode. Additional details of the GC/MS method can be found in Hladik and others (2008, 2009).

4.1.2. Water by LC/MS/MS

Each 1-L filtered-water sample will be spiked with the recovery surrogate standards monuron (Chem Service, West Chester, Pennsylvania) and imidacloprid-d_4 (Cambridge Isotope Laboratories, Andover, Massachusetts). The sample is then pumped under vacuum at a flow rate of 10 mL/min through an Oasis HLB SPE (6 mL, 500 mg, 60 µm, Waters Corporation, Milford, Massachusetts) cartridge that has been cleaned with one column-volume of DCM, followed by one column-volume of acetone and two column-volumes of deionized water. The SPE cartridge is then dried using a stream of carbon dioxide for approximately 1 hour or until the SPE sorbent is dry. The cartridges are eluted into a clean, glass concentrator tube by using 10 mL of a solution of 1 DCM:1 acetone. The eluent is then evaporated to less than 0.5 mL in a fume hood under a gentle stream of nitrogen, then solvent-exchanged into acetonitrile and further evaporated to 200 µL. The internal standard ($^{13}C_3$-caffeine, Cambridge Isotope Laboratories) is then added (20 µL of a 0.5-ng/µL solution). The sample extracts will be stored (not to exceed 30 days) in a freezer at –20 °C until analysis.

Water extracts will be analyzed for the herbicide diuron, three diuron degredates (DCPMU, 3,4-Dichlorophenylurea (DCPU), and 3,4-dichloroaniline), and six neonicotinoid insecticides (acetamiprid, clothianidin, dinotefuran, imidacloprid, thiacloprid, and thiamethoxam) by LC/MS/MS. Aliquots of the sample extracts (10 µL) are injected, and the compounds are separated on an Agilent (Palo Alto, Calif.) 1260 Series bio-inert high performance liquid chromatograph (HPLC) coupled to a 6430

tandem mass spectrometry (MS)system with a Zorbax Eclipse XDB-C18 column (2.1 mm × 150 mm × 3.5 mm, Agilent). The mobile phases are acetonitrile and 5 millimolar (mM) formic acid in water. Data are collected in the multiple-reaction-monitoring mode. Additional details of the LC/MS/MS analytical method can be found in Hladik and Calhoun (2012).

4.1.3. Suspended Sediment by GC/MS

Filter papers will be extracted by sonication. Each filter paper will be weighed to determine the amount of suspended sediment, placed in an Erlenmeyer, and spiked with 50 µL of a 2 µL surrogate solution containing the recovery surrogates N-propyl-d_{14} trifluralin, phenoxy-$^{13}C_6$-*cis* permethrin, and ring-$^{13}C_{12}$-4,4'-DDE (Cambridge Isotope Laboratories, Andover, Massachusetts). A 1:1 mixture of acetone/DCM will be added to the Erlenmeyer until the filter is submerged then placed in a sonicator for 20 minutes. The extract will then be decanted through sodium sulfate into a clean collection vessel while leaving the filter and sediment behind. The Erlenmeyer will be sonicated again with a fresh addition of the acetone/DCM mixture for another 20 minutes and decanted into the same vial. This is blown down under a stream of nitrogen to 200 µL. An internal standard (20 µL of 2 nanograms per liter [ng/L]) containing the deuterated polycyclic aromatic hydrocarbon compounds acenaphthene-$d_{10,}$ phenanthrene-d_{10} and pyrene-d_{10} are then added to each sample. The sample extracts are then stored (not to exceed 30 days) in a freezer at –20 °C until instrumental analysis.

SECTION B5. QUALITY CONTROL

A number of quality-control checks will be implemented to assess whether data quality objectives are being met (Table 6). These quality control checks measure accuracy, precision, bias, and extraction efficiency and are listed in Table 6 for water and sediment samples. All quality-control checks meet or exceed SWAMP requirements; therefore the data generated are comparable to other data that adhere to SWAMP requirements.

Accuracy will be measured and controlled by ensuring proper calibration and verification, the use of reference material, matrix spikes, surrogate spikes, and internal standards. Precision will be measured by analyzing field replicates and matrix spike replicates. Bias will be assessed by collecting field and laboratory blanks, using reference material and internal standards, and analyzing surrogate spike and matrix spike samples. Extraction efficiency will be assessed by matrix spikes and surrogate spikes.

QC data will be inspected by the PI as it becomes available during the course of the project. If any data indicates that quality objectives are not being met the PI will consult with the CoPI, LM and PD to determine if the failure is most likely due to field or laboratory procedures/methods. If it is determined that field methods are the likely cause, the PI and PD will work with the respective collecting entity to ensure that SWAMP protocols are being followed correctly and if any additional protocols (specific to this

project) need to be implemented. If it is determined that laboratory procedures are the likely cause then the PI will work with the CoPI and LM to ensure that proper procedures as outlined in the QAPP are being implemented and to develop any additional procedures to bring QA sample results in line with data quality objectives. In each case, any changes to field or laboratory procedures will be documented and addressed in the final report.

Table 6 QC sample types and data quality objectives for water and sediment samples

Laboratory QC Sample Type	Frequency of Analysis	Data Quality Objective	Data Quality Indicator
Calibration	At each instrument set up, major disruption, and when routine calibration check exceeds specific control limits.	Linear regression, $r^2 > 0.995$ using an 7 point calibration curve ranging from 0.01 to 1 ng/uL	Accuracy
Calibration Verification	After initial calibration or recalibration. Every 6 samples.	Recovery = 75 - 125%	Accuracy
Laboratory Blanks	One method blank per 20 samples or one per batch, whichever is more frequent. Laboratory blanks should comprise 10 % of all samples per sampling event.	Blanks < MDL for target analyte.	Bias
CRM (Reference Material)	National Water Quality Laboratory Schedule 2003/2033 (1 μg/mL) spiked into 1 L sample water (GC/MS). Routine accuracy assessment every 20 samples	Measured value < 95% confidence intervals, if certified. Otherwise, recovery = 50-150%.	Accuracy, bias
Matrix Spikes	One per 20 samples or one per batch, whichever is more frequent.	Recovery = 70-130%	Extraction efficiency, accuracy, bias
Matrix Spike Replicate	One per 20 samples or one per batch, whichever is more frequent.	Recovery = 70-130% RSD < 25% between replicates	Extraction efficiency, precision, bias
Surrogate Spikes	Isotopically labeled compounds added to every sample	% Recovery = 70-130%	Extraction efficiency, accuracy, bias
Internal Standards	Isotopically labeled compounds added to every sample	% Recovery = 70-130%	Sensitivity, accuracy, bias
Field Blanks	One per 20 samples or one per each sampling entity, whichever is more frequent	Blanks <MDL for target analyte.	Bias
Field Replicate	Replicates should comprise 5 % of total project sample count or one per each sampling entity, whichever is more frequent	RSD < 25% for replicates.	Precision

SECTION B6. INSTRUMENT/EQUIPMENT TESTING, INSPECTION AND MAINTENANCE

Proper maintenance procedures for instruments and equipment will be followed and documented. To ensure that equipment is operating properly and that data quality is high, the USGS laboratory staff will employ quality assurance, quality control, and corrective measures. These measures will include the following:

Reference standards and instrument blanks will be analyzed periodically, using the same procedures as are used for the environmental samples during GC-MS analyses. A standard should be analyzed after every tenth sample injection to verify that the analyte calibration curves are within operational specifications. If the measured concentrations of the standards differ by more than 25 % from expected concentrations, the corresponding environmental samples should be re-analyzed after the source of the problem is determined and corrected. A blank shall be run after each reference standard to verify absence of sample carryover or contamination of the instrument.

SECTION B7. INSTRUMENT/EQUIPMENT CALIBRATION AND FREQUENCY

Initial calibration curves will be generated on each instrument (GC/MS and LC/MS/MS) using standard solutions containing all of the target pesticides before sample analysis begins. Computer software will be used to generate linear regression equations for pesticide response over the concentration range of the calibration curve (0.01-1 ng/µL for GC/MS and 0.01-1.0 ng/µL for LC/MS/MS). Calibration curves will be accepted when the correlation coefficient is greater than 0.99. Calibration will be checked frequently by analyzing standards throughout the sample analysis, but at the very least once every 8 hours during the sample analysis period. Pesticide quantification in the environmental samples will continue as long as the calibration curves are verified to be acceptable.

SECTION B8. INSPECTION/ACCEPTANCE OF SUPPLIES AND CONSUMABLES

Supplies and consumables will be purchased through local vendors, scientific supply houses, or USGS centralized warehouses. They will be deemed acceptable unless inspection reveals lack of compliance with expected criteria. For example, any solvents that are used will be expected to be of pesticide grade or better as indicated on the label. Containers, such as cleaned and oven-baked pesticide bottles, supplied through USGS centralized warehouses are periodically checked to confirm absence of pesticide residues. All chemicals are dated upon receipt. All supplies are stored appropriately and are discarded upon the expiration date.

SECTION B9. NON-DIRECT MEASURES

Sites to be sampled in this study have been sampled in the recent past for toxicity and pesticides (though not all compounds analyzed for during this study). Previous samples have been collected by various State entities following SWAMP compliant methods and procedures. Relevant data collected from these earlier sampling events may be incorporated in this study, pending data validation and quality assessment. Criteria for accepting previously collected data include representativeness of similar conditions, documented bias, methods of data evaluation, applicability to this project, and data summarization.

SECTION B10. DATA MANAGEMENT

All data will be maintained and managed as established in Section A9.

SECTION C1. ASSESSMENTS AND RESPONSE ACTIONS

The PD or her designee may conduct inspections of the physical facilities, operational systems and operating procedures at USGS OCRL. The facility requests a 24-hr notice prior to the inspections.

If an audit discovers discrepancies or protocol deviations, the PD or designee will discuss the observed discrepancy with the person(s) responsible for the activity (see organizational chart). The appropriate parties will discuss the accuracy on the information collected, the cause(s) of deviation(s), possible impact(s) on data quality and possible corrective actions.

1.1 Deviations and corrective actions

Surveillance of records and overall project status will be conducted by the PI. Surveillance will be conducted following each sampling event, and after laboratory results have been received.

The PI will perform a technical systems audit. During this audit, the PI will examine field activities and record-keeping procedures to assess their conformance to the QAPP. This audit will take place after each sampling trip. Any non-conformance with the QAPP will be corrected, documented, and reported to the PD. The laboratory's QA procedures and QC results for this project also will be reviewed. Laboratory performance will be assessed using quality-control samples, namely field blanks, replicate samples, and matrix-spike samples.

Prior to preparing a final report, an audit of data quality will be performed to assess data management, and if necessary correct any errors in the project database. Statistical tools will be utilized to determine: (a) if the data satisfy the assumptions of the data-quality objectives and sampling design, and (b) whether the total error in the data is tolerable.

SECTION C2. REPORTS TO MANAGEMENT

The following products will be delivered by USGS:

1. USGS will provide brief semi-annual reports to the CVRWQCB PD which will include a summary of completed activities and data results in tabular form summarizing pesticide analyses of project samples completed during the previous quarter (subject to USGS PI and QAO approval and release of the data).

2. A final report will be prepared to include a description of the project design, and analytical methods along with results of all environmental and QA/QC sample analyses. A preliminary draft of the data report should be submitted to the CVRWQCB by March 1, 2017. Comments on the draft data report should be submitted by March 31, 2017. The data report will be finalized by June 30, 2017.

Table 7 Schedule of reporting requirements

Task	Due Date
Semi-annual Progress Reports	June 30, 2015; semi-annually thereafter
Draft Final Report	January 1, 2017
Draft Final Report: Reviewer Comments	March 1, 2017
Final Report	June 30, 2017

SECTION D1. DATA REVIEW, VERIFICATION AND VALIDATION

Data generated by project activities will be reviewed against the data quality objectives listed in Table 6. Data will be separated into three categories:

1. Data meeting all data quality objectives
2. Data meeting data quality objectives but failing to meet precision criteria
3. Data failing to meet accuracy criteria

Data meeting all data quality objectives but failing to meet QA/QC criteria will be flagged until the impact of the failure on data quality is determined. Once determined, the data will be moved into either the first category or the third category. Data falling in the first category is considered usable by the project. Data falling in the third category is considered not usable. Data falling in the second category will have all aspects assessed. If sufficient evidence is found supporting data quality for use in this project, the data will be moved to the first category, but appropriately flagged.

SECTION D2. VERIFICATION AND VALIDATION METHODS

The USGS PI will review field notes and field data for each sampling event to verify that the sampling design was followed (i.e., spatial distribution of sampling locations, sample collection protocol). Departures from the sampling design will be considered in the design of each subsequent sampling event. Deviations may be necessary to better characterize the system, or to accommodate unforeseen field conditions. Significant departures in sampling design (e.g., changes in sampling sites or sample collection procedures) will be noted in the project database, audit of data quality, and final report. The PI and QAO will evaluate: (a) the effects of all deviations (if any) on overall data completeness, and (b) data usability for supporting conclusions. Changes in sampling design must adhere to data quality objectives as outlined in this document, and original and modified methods should produce directly comparable results as supported in accepted literature.

Field records, technical systems audits, and project surveillance will be used to verify proper sample collection and equipment decontamination procedures. Analytical results for equipment blanks also may verify proper equipment decontamination. All of this information will be considered in the final audit of data quality. Departures from sample collection and equipment decontamination procedures that would be considered unacceptable include the use of contaminated sampling bottles, lack of critical sample collection information, cross-contamination or incorrect identification of samples.

Potential departures from the sample handling and custody procedures will be determined by reviewing chain of custody forms and laboratory analysis forms. For data to be considered valid the chain of custody forms for all samples must be in the possession of the Project Manager and strict adherence to holding times and temperatures must be followed.

Validation of laboratory data will be performed in the audit of data quality by assessing the results of QC sample analyses. Laboratory data will be validated for precision, accuracy, and completeness according to the criteria discussed earlier. At the discretion of the PI, data that do not meet these requirements will either not be reported or will be reported with an explanation of any necessary conditions.

SECTION D3. RECONCILIATION WITH USER REQUIREMENTS

The analytical data generated by this project is the product of a reconnaissance, as opposed to a monitoring, study and hence does not lend itself to complex statistical interpretation. This study does not require complex statistical analysis because of the relatively small number of samples that will be collected at each site. The only use of statistics will be 1) in ascertaining the adequacy of the instrument blanks and spike recoveries, and 2) in comparing duplicate (replicate) analyses for selected field samples. “Replicate” data are generated whenever splits from a sample or blank are processed separately, and whenever the isolate from processing is injected into the instrument more

than once. Criteria, in terms of percent difference for acceptance of results based on these replicate analyses are discussed in earlier sections. The contract deliverables will be used to determine which pesticides are detected in surface water and if any are present above known toxicity values, to prioritize which pesticides, if any, warrant further investigation, and to evaluate models and monitoring protocols.

LIST OF ACRONYMS AND ABBREVIATIONS

PD	Contract Manager
COC	Chain of Custody
CVRWQCB	Central Valley Regional Water Quality Control Board
LM	Laboratory Manager
PI	Principal Investigator
QA/QC	Quality Assurance/Quality Control
QAO	Quality Assurance Officer
QAPP	Quality Assurance Project Plan
SOP	Standard Operating Procedures
SWRCB	State Water Resources Control Board

REFERENCES

Hladik, M.L., and Calhoun, D.L., 2012, Analysis of the herbicide diuron, three diuron degradates, and six neonicotinoid insecticides in water—Method details and application to two Georgia streams: U.S. Geological Survey Scientific Investigations Report 2012–5206, 10 p.

Hladik, M.L., Smalling, K.L., and Kuivila, K.M., 2008, A multi-residue method for the analysis of pesticides and pesticide degradates in water using Oasis HLB solid phase extraction and gas chromatography-ion trap mass spectrometry: Bulletin of Environmental Contamination and Toxicology, v. 80, p. 139–144.

Hladik, M.L., Smalling, K.L., and Kuivila, K.M., 2009, Methods of analysis: Determination of pyrethroid insecticides in water and sediment using gas chromatography/mass spectrometry: U.S. Geological Survey Techniques and Methods book 5, chap. C2, 18 p.

Appendix A

U.S.EPA
Aquatic Life Benchmark Values

OPP Aquatic Life Benchmarks (µg / L)										
(freshwater)										
Pesticide	**Year Updated**	**CAS number**	**Fish**		**Invertebrates**		**Nonvascular Plants**	**Vascular Plants**	**Office of Water**	
									Aquatic Life Criteria	
			Acute1	Chronic2	Acute3	Chronic4	Acute5	Acute6	**Maximum Concentration (CMC)**	**Continuous Concentration (CCC)**
2,4-D	2014	94-75-7			12500					
2,4-D acids and salts		94-75-7	12075	14200	12500	16050	3880	13.1		
2,4-D esters		.	130	79.2	1100	200	66	330		
2,4-D, 2-ethylhexyl ester	2014	1928-43-4		79.2	1700		152	330		
2,4-D, Butoxyethyl ester	2014	1929-73-3	214			200				
2,4-D, Diethanolamine salt	2014	5742-19-8	> 40800			16050		299.2		
2,4-D, Dimethylamine salt	2014	2008-39-1	1E+05	23600			3880			
2,4-D, Isopropyl ester	2014	94-11-1	130		1100					
2,4-DB		94-82-6	1000		7500		932			
2,4-DB-DMAS		2758-42-1	1567		10150					
3, 6-dichlorosalicylic acid (DCSA)		3401-80-7	> 50000		44500		138000	> 73000		
3-chloroacrylic acid degradate of Telone		.	34750		27500		430	220		

3-chloroallyl alcohol degradate of Telone		.	493		1150		32900	1694		
3-Trifluoromethyl-4-Nitrophenol (TFM)		88-30-2	300		1900		1200			
Abamectin	2014	71751-41-2	1.6	0.52	0.17		> 100000	3900		
Acephate		30560-19-1	4E+05	5760	550	150	> 50000			
Acequinocyl		57960-19-7	33500	520	1.2	0.98	960			
Acetamiprid	2013		> 50000	19200	10.5	2.1	> 1000	> 1000		
Acetochlor		34256-82-1	190	130	4100	22.1	1.43	3.4		
Acetochlor degradate ethanesulfonic acid (ESA)		187022-11-3	> 90000		> 62500		9900			
Acifluorfen sodium		62476-59-9	8500	< 1500	14050		> 265	378		
Acrolein		107-02-8	7	11.4	> 15.5	7.1	28	72	3	3
Alachlor		15972-60-8	900	187	1250	110	1.64	2.3		
Alachlor ethane sulfonic acid		.	> 52000		> 52000					

Alachlor oxanilic acid		.	> 500000		> 47500					
Aldicarb		116-06-3	26	0.46	10	1	> 5000			
Aldicarb sulfone		1646-88-4	21000		140					
Aldicarb sulfoxide		1646-87-3	3570		21.5					
Aliphatic Oils- 100 Paraffine Oil		64742-54-7	> 50000		205					
Aliphatic Oils- 70 Orchard Spray		64742-55-8			1200					
Aliphatic Oils- 90 Neutral Oil		8012-95-1	> 50000		10					
Aliphatic Oils- GB-1111		.	> 60000		50					
Aliphatic Oils- N65DW		.	> 250000000							
Aliphatic Oils- VHVI-4		.	> 38000		< 450					
Allethrin		584-79-2	9.5		1.05					
Alpha-cypermethrin	2014	67375-30-8	1.1	0.14	0.0018	0.00059	> 33.5	> 1.39		
Alpha-cypermethrin degradate (3-phenoxybenzoic acid) 3-phenoxybenzoic acid	2014		6650		44500					
Aluminum Phosphide	2014	20859-73-8								

Ametryn	2014	834-12-8	1800	700	14000	240	3.67	13		
Aminocyclopyrachlor acid	2013	858956-08-8	> 60000	11000	19850	< 370	7400	> 122000		
Aminocyclopyrachlor ester	2013		6500		9950					
Aminopyralid	2013	150114-71-9	> 50000	1360	> 49300	102000	18000	> 88000		
Amitraz		33089-61-1	170	> 1.5	17.5	1.1				
Amitraz BTS 27271		33089-61-1	14200		1295					
Amitraz BTS 27919		33089-61-1	33100		> 50000					
Ancymidol	2014	12771-68-5			> 48200			292		
Antimycin A		1397-94-0	0.005		0.004					
Arsenic Acid	2014	7778-39-4	25000		7500		9.2	> 9800		
Arsenic Trioxide	2014	1327-53-3	12800							
Asulam sodium		2302-17-2	> 87500		13550		180	140		
Atrazine	2014	1912-24-9	2650		360	60	< 1	0.001		
Azinphos methyl		86-50-0	0.18	0.055	0.08	0.036				
Azoxystrobin		131860-33-8	235	147	130	44	49	3400		
Benfluralin		1861-40-1	34.85	1.9	1090	15.5	> 100			

Bensulide		741-58-2	360	374	290		1500			
Bentazon		25057-89-0	> 50000		> 50000		4500	5350		
Bentazon, sodium salt		50723-80-3	> 50000		31150		60	5350		
Bifenazate	2014	149877-41-8	290		250	150	890	> 3820		
Bifenazate degradate D1989	2014	149877-41-8			125					
Bifenazate degradate D-3598	2014	149877-41-8	22		25.5		780			
Bifenazate degradate D-9472	2014	149877-41-8	115		390		710			
Bifenthrin		82657-04-3	0.075	0.04	0.8	0.0013				
Bioallethrin		28057-48-9	4.7							
Bispyrabac sodium	2013	125401-92-5	> 51000	9200	> 49600	110000	250	12		
Boric Acid Salts		10043-35-3	> 400000		66500					
Boscalid		188425-85-6	1350	116	> 533	298	1340	3900		
Bromacil		314-40-9	18000	3000	60500	8200	6.8	45		
Bromoxynil	2014	1689-84-5								
Bromoxynil Heptanoate	2014	56634-95-8	14.5		15.5			219		
Bromoxynil Octanoate	2014	1689-99-2		18	5.5	2.5	51			

Bromoxynil phenol		1689-84-5	1050		9610					
Butylate		2008-41-5	105		5950					
Cacodylate Acid	2014	75-60-5	8500		9050			30900		
Captan	2014	133-06-2	13.1	16.5	4200	560	320	> 12700		
Captan degradate (1,2,3,6-Tetrahydrophthalimide)	2014	1469-48-3	> 60000		> 56500		> 181000			
Captan degradate (tetrahydrophthalimic acid)	2014		> 63000							
Carbaryl		63-25-2	110	6	0.85	0.5	660	1500	2.1	2.1
Carbendazim	2013	10605-21-7								
Carbofuran		1563-66-2	44	5.7	1.115	0.75				
Carboxin		5234-68-4	600		42200		370	670		
Chlorantraniliprole		500008-45-7	> 600	110	4.9	4.5	1800	2000		
Chlorfenapyr		122453-73-0	3.72	3.68	2.915	3.57				
Chlorfenapyr Metabolite CL303094		.			280					
Chlorfenapyr Metabolite CL303195		.			850					

Chlorfenapyr Metabolite CL303267		122454-23-3	35		53.5					
Chlorfenapyr Metabolite CL312094		122453-73-0	> 464							
Chlorfenapyr Metabolite CL325195		122453-73-0	1050							
Chlorflurenol methyl ester		2536-31-4								
Chlormequat chloride		999-81-5	> 50000		8450	5000	> 207000	2800		
Chloropicrin	2014	76-06-2	5.5		60			6.5		
Chlorothalonil		1897-45-6	5.25	3	1.8	0.6	6.8	630		
Chlorothalonil degradate (SDS-3701)		.	4600		13000		33700			
Chlorpyrifos		2921-88-2	0.9	0.57	0.05	0.04	140		0.083	0.041
Chlorpyrifos-methyl		5598-13-0	7		0.085					
Chlorsulfuron	2014	64902-72-3	> 150000	32000	> 185000	20000	50	0.35		
Chromated Arsenicals	2014					< 0.95				
Clethodim		99129-21-2	7500		2850		11000	1100		

Clodinafop-propargyl	2014	105512-06-9	120		> 1000		3000	> 2400		
Clodinafop-propargyl Degradate (CGA-193469)	2014	114420-56-3			> 4600	2600				
Clodinafop-propargyl Degradate (CGA-302371)	2014	514797-96-7	> 47700		> 49450		30600			
Clofentezine		74115-24-5	> 7.3	6	> 40	26.2				
Clomazone		81777-89-1	1450	350	2700	2200	167	30200		
Clopyralid		1702-17-6	1E+06		56500					
Clothianidin	2013	210880-92-5	> 50750	9700	11	1.1	64000	121000		
Copper		7440-50-8	15.7	9.01	2.05	1.11	3.1	2300		
Coumafos		56-72-4	140	11.7	0.037	0.037				
Coumaphos	2014	56-72-4	140	11.7	0.037	0.0337				
Cyanamide		420-04-2	23000	< 507	1650	100	650	2330		
Cyantraniliprole	2014	736994-63-1	> 5000	10700	10.2	6.56	> 10000	12100		
Cyazofamid	2013	120116-88-3	> 53.5	90.1	> 650	< 87		> 1220		
Cycloate		1134-23-2	2250		1300					
Cyfluthrin	2013	68359-37-5	0.034	0.01	0.0125	0.0074	> 181			
Cyfluthrin, beta	2013	68359-37-5	0.034		0.145					
Cyhexatin		13121-70-5								

Cypermethrin		52315-07-8	0.195	0.14	0.21	0.069				
Cyphenothrin		39515-40-7	0.17		0.215					
Cyprodinil		121552-61-2	1205	230	16	8	2250			
Cyromazine		66215-27-8	> 44850	14000	> 46400	310				
Dacthal (DCPA)		1861-32-1	15000		13500		> 11000	> 11000		
Daminozide		1596-84-5	2E+05		35500		> 99800			
Dazomet	2014	533-74-4								
Dazomet (degradate methyl isothiocyanate (MITC))		533-74-4	25.6		27.5	25	254	590		
Dazomet degradate (Methyl Isothiocyanate)	2014	556-61-6	26.5		27.5	25	200	590		
Deltamethrin		52918-63-5	0.29	0.017	0.055	0.0041				
Diazinon		333-41-5	45	< 0.55	0.105	0.17	3700		0.17	0.17
Dicamba acid		1918-00-9	14000		> 50000		61	> 3250		
Dicamba, dimethylamine salt		2300-66-5	5E+05		781500					
Dicamba, sodium salt		1982-69-0	3E+05		17300					

Dichlobenil		1194-65-6	2465	< 330	1850	560	1000	30		
Dichloroprop (2,4-DP)	2013	120-36-5								
Dichlorvos (DDVP)		62-73-7	91.5	5.2	0.035	0.0058	14000			
Dicofol		115-32-2	26.5	4.4	70	19	> 5000			
Dicrotophos		141-66-2	3150		6.35	0.99				
Difenacoum		56073-07-5	32		305		320			
Difenoconazole	2013	119446-68-3	405	8.7	385	5.6	98	1900		
Difenzoquat methyl sulfate		43222-48-6	23250		1265		630	120		
Difethialone		104653-34-1	25.5		2.2					
Diflubenzuron		35367-38-5	64500	100	0.0014	0.00025	200	190		
Dimethenamid		87674-68-8	3150	300	6000	1020	14	8.9		
Dimethoate		60-51-5	3100	430	21.5	0.5	84			
Dimethomorph	2014	110488-70-5	3100	< 341	> 5300	110				
Dinotefuran	2013	165252-70-0	> 49550	> 6360	> 484150	> 95300	> 97600	> 110000		
Dinotefuran degradate dn phosphate	2013				> 55300		> 100400			
Dinotefuran degradate MNG	2013						> 98700			
Diquat Dibromide		85-00-7	7400	122	385	< 36	9.4	0.75		

Disulfoton		298-04-4	19.5	4	1.95	0.01				
Disulfoton sulfone		######	> 4600		17.5	0.14				
Disulfoton sulfoxide		######	30000		32	1.53				
Dithiopyr	2013	97886-45-8								
Diuron		330-54-1	200	26.4	80	200	2.4	15		
Dodine		######	285	99	8.9	7.3	0.95			
DSMA	2014	144-21-8					1500			
Dyes + Acids		.	> 48000	> 96000	> 48500					
Endosulfan		115-29-7	0.05	0.11	0.3	0.01	428		0.22	0.056
Endosulfan sulfate		1031-07-8	1.9		150					
Endothall (acid)		145-73-3	24500	1300	46000	< 2200				
Endothall (dipotassium salt)		2164-07-0	4576	1790	31900			610		
Endothall (N,N-dimethylalkylamine salt)		66330-88-9	7.5	56	6	2.3	2.3	740		
EPN	2013	2104-64-5								
EPTC	2014	759-94-4	7000		3250	800	1400	5600		
EPTC (S-Ethyl dipropylthiocarbamate)		759-94-4	7000		3245	810	1400	5600		

Esbiol (s-bioallethrin)		28434-00-6	3.95							
Esbiothrin		84030-86-4			4.45					
Esfenvalerate		66230-04-4	0.035	0.035	0.025	0.017				
Ethalfluralin		55283-68-6	16	0.4	30	24	25			
Ethephon		16672-87-0	44000		15850	17000	23500	2500		
Ethion	2013	563-12-2								
Ethofumesate	2013	26225-79-6	8750	2560	147000	300	> 2760			
Ethoprop		13194-48-4	150	24	22	0.8	8400			
Etofenprox		80844-07-1	1.35	23	0.4	0.17	> 18.8	> 26		
Etoxazole	2013	153233-91-1	> 150	15	3.55	0.13				
ETU (common degradate of Mancozeb and Maneb)		.	> 251000	37320	134500	2				
Fenamidone	2013	161326-34-7	370	< 8.6	24.5	12.5	70	> 880		
Fenamiphos		22224-92-6	4.75	3.8	0.95	0.12				
Fenarimol		60168-88-9	450	180	3400	113	100			
Fenbutatin- oxide		13356-08-6	0.85	0.31	15.5	16				

Fenhexamid	2014	126833-17-8	670	101	> 9400	1000	4820	> 2300		
Fenitrothion		122-14-5	860	46	1.15	0.087				
Fenoxaprop-p-ethyl		71283-80-2	155	22	> 529		430	> 3000		
Fenoxycarb		72490-01-8	800	48	200	0.0016				
Fenpropathrin		39515-41-8	1.1	0.091	0.265	0.064				
Fenpyrazamine	2014	473798-59-3	2600	370	2750	340	11	1100		
Fenpyrazamine degradate-2-Cyano-N-isopropyl-2-(otolyl)acetamide (MCNI)	2014				> 25000					
Fenpyrazamine degradate-5-Amino-2-isopropyl-4-(o-tolyl)-1H-pyrazol-3-one(S-2188-DC)	2014		> 44500		> 47000		32000			
Fenpyrazamine degradate-5-Amino-4-hydroxy-2-isopropyl-4-(o-tolyl)pyrazol-3-one(S-2188-OH)	2014		> 48500		> 49000		55000			
Fenpyroximate	2013	134098-61-6	0.22	0.11	0.8	0.56	1.9	> 190		
Fenthion		55-38-9	415	7.5	2.6	0.013	400	> 2800		
Fipronil		120068-37-3	41.5	6.6	0.11	0.011	140	> 100		
Fipronil degradate MB45950		.	41.5	6.6	1.065	0.11	140	> 100		
Fipronil degradate MB46136		.	12.5	0.67	0.36	0.037	140	> 100		
Fipronil degradate MB46513		.	10	0.59	100	10.3	140	> 100		

Florasulam		145701-23-1	> 50000	119000	> 146000	38900	3.45	1.18		
Fluazinam	2014	079622-59-6	18	0.69	90	68	1.1			
Flubendiamide		272451-65-7	> 32.55	60.5	> 27.4	41.5	> 69.3	> 54.6		
Fludioxonil		131341-86-1	235	19	450	< 19	70	> 1000		
Flumetsulam	2014	98967-40-9	> 146500	197000	127000	111000	3.21	3.1		
Flumiclorac-pentyl		87546-18-7	550		> 19000					
Flumioxazin	2013	103361-09-7	1150	7.7	2750	28	0.83	0.49		
Fluometuron		2164-17-2	320		110		30	220		
Fluopicolide	2014	239110-15-7	174.5	151	> 850	190	< 1.4	> 3200		
Fluopicolide degradate- 3-chloro-5-trifluoromethylpyridine-2-carboxylic acid	2014	239110-15-7	51000							
Fluopicolide degradate-BAM	2014	239110-15-7	1E+05	10000	92050	320000	> 10000			
Fluridone		59756-60-4	2800	480	650					
Fluroxypyr		69377-81-7	7150		> 50000		> 100000			
Fluroxypyr MHE		81406-37-3	6600		> 54.5	60	290	> 2300		

Flurprimidol		56425-91-3	8600	944	5900	2960	840	10400		
Flutolanil		66332-96-5	1250	233	> 3400	530	8010	8010		
Flutriafol	2013	76674-21-0	16500	4800	33550	310	460	780		
Folpet	2014	133-07-3	7.5	8.8	10					
Fomesafen Sodium		108731-70-0	63000	9400	188000	50000	92	210		
Foramsulfuron	2014	173159-57-4	> 50000	10500	> 51250	100000	3300	0.65		
Formetanate HCl		23422-53-9	1350	480	45	0.5				
Fosamine Ammonium		25954-13-6	2E+05		762000		> 15000	> 21000		
Fosthiazate	2014	98886-44-3	55500	2320	130	61	> 4510			
Gamma-cyhalothrin		76703-62-3	0.015		0.0002		> 2850			
Glufosinate	2014	77182-82-8	> 156000	50000	325500	31000	72	1470		
Glufosinate ammonium		77182-82-2	> 160000		334000	32000	7800	1470		
Glufosinate degradate 2-acetamido-4-methylphosphinico-butanoic acid (NAG)	2014	77182-82-8	> 50450				> 357000			
Glufosinate degradate 2-methylphosphinico-acetic acid (MPA)	2014	77182-82-8	> 49450		18500		53000	> 97200		

Glufosinate degradate 3-methylphosphinicopropionic acid (MPP)	2014	77182-82-8	> 50000	26000	21000	< 6430	> 1000000	> 103000		
Glufosinate degradate Methylphosphinico-formic acid (MPF)	2014	77182-82-8	> 51000		> 49100		> 94800			
Glyphosate		1071-83-6	21500	1800	26600	49900	12100	11900		
Glyphosate degradate aminomethyl phosphoric acid (AMPA)		1066-51-9	2E+05		341500					
Glyphosate isopropylamine salt		38641-94-0	34700							
Hexaflumuron		86479-06-3	> 127.8		0.0555					
Hexazinone		51235-04-2	1E+05	17000	75800	20000	7	37.4		
Hexythiazox	2014	78587-05-0	> 60			6.1	> 120	> 120		
Hydramethylnon		67485-29-4	45		570					
Hymexazol		10004-44-1	> 50000		15400		40900	8800		
Imazamox		114311-32-9	> 59500		> 61000		> 40	11		
Imazapic acid	2013	104098-48-8	> 50000	96000	> 50000	96000	> 44.1	6.1		
Imazapic ammonium	2013									
Imazapyr		81334-34-1	> 50000	43100	> 50000	97100	12200	24		

Imazethapyr (ammonium salt)	2013	81335-77-5	1E+05		500000		59200			
Imazethapyr CL266858	2013									
Imazethapyr CL271197	2013									
Imazethapyr CL290084	2013									
Imazosulfuron	2013	122548-33-8	> 34500	2900	> 45500	840	206	1.46		
Imazosulfuron degradate (IPSN)	2013					11000		> 113000		
Imidacloprid		138261-41-3	> 41500	1200	34.5	1.05	> 10000			
Indoxacarb	2014	173584-44-6	145	150	300	75	> 110	> 84		
Indoxacarb degradate (IN-JT333)	2013		12	5.5	> 14.5	3.6				
Indoxacarb degradate- (IN-JT333) (methyl-7-chloro-2,5-dihydro -2-[[[4(trifluoromethoxy)phenyl]amino]carbonyl]indeno[1,2e][1,3,4]oxadiazine -4a(3H)-carboxylate)	2014		12	5.5	> 14.5	3.6				

indoxacarb degradate (IN-MP819)	2013		> 184	84.9	32	8				
Indoxacarb degradate- (IN-MP819) (Indenol[1 ,2-e][1 ,3,4]oxadlazine-1 (2H)-carboxylic acid, 7-chloro-3,5-dlhydno-2-[[[4-(triftuoromethoxy)phenyl]amino]carbonyl]-, methyl ester)	2014		> 184	84.9	32	8				
Indoxacarb degradate (KN127)	2013		197							
Iodomethane		74-88-4	665		285					
Iodosulfuron-methyl-sodium	2014	144550-36-7	> 44050	10200	> 43450	9100	41	0.7		
Iodosulfuron-methyl-sodium Degradate (Metsulfuron)	2014	74223-64-6	> 75000	4500	> 75000	100000	31	0.36		
Ipconazole		125225-28-7	765	0.18	850					
Iprodione	2014	36734-19-7		260	120		> 130	> 12640		
Isoxaben		82558-50-7	> 550	400	> 650	690	> 1400			
Isoxaflutole		141112-29-0	> 850		> 750		110	4.9		

Isoxaflutole - rpa202248 (degradate)		.	> 15300		> 29800		5000	75		
Kresoxim methyl		143390-89-0	95	87	166	55	29.2	> 305		
Kresoxim-methyl	2014	143390-89-0	95	87	166	55	29.2	> 301		
Kresoxim-methyl degradate (BF490-1)	2014		> 52000		> 50000					
Lactofen		77501-63-4	230	1.4	2425		0.99	0.6		
Lambda-cyhalothrin		91465-08-6	0.105	0.031	0.0035	0.002	> 310			
Limonene		138-86-3	40000		19500					
Lindane (gamma HCH)		58-89-9	0.85	2.9	0.5	54			0.95	
Linuron		330-55-2	1500	5.58	60	0.09	13.7	2.5		
Magnesium phosphide										
Malathion	2013	121-75-5	16.5	8.6	0.295	0.035	2400	> 9630		0.1
Mancozeb		###### #	230		290		47			
Mandipropamid		374726-62-2		220	3550		> 2500	> 7900		
Maneb		12427-38-2	21		60		13.4			
MCPA acid		94-74-6					300	170		
MCPA DMAS		2039-46-5	48000	12000	41000	11000	160	130		

MCPA EHE		29450-45-1	380		90		170	20		
MCPA sodium salt		3653-48-3	> 34000		> 92000					
MCPB sodium salt		6062-26-6	1950		25000		380	210		
Mecoprop (MCPP)-P acid		16484-77-8			> 45500	50800				
Mecoprop (MCPP)-P DMAS		66423-09-4	> 46500				14	1300		
Mefenoxam		70630-17-0	> 60500		20950	100		77000		
Mesosulfuron-methyl	2014	208465-21-8	> 45750	29600	> 45100	1700	2400	0.64		
Mesosulfuron-methyl degradate (F092944) (2-Amino-4,6-dimethoxypyrimidine)	2014		48500		> 50000	24000	120000	> 100000		
Mesosulfuron-methyl degradate (F147447) (6-Methanesulfonamidomethyl- 1,2-benzisothiazol-3(2H)-one 1,l dioxide)	2014						> 92000	> 90900		
Mesosulfuron-methyl degradate (F160459) (Methyl 2-[3-(4-hydroxy-6-methoxypyrimidine-2-yl)ureidosulfonyl]-4-methanesulfonamido-methyl benzoate)	2014						98000	1500		
Mesosulfuron-methyl degradate (F160460) (2-[3-	2014							> 94710		

(4-hydroxy-6-methoxypyrimidin-2-yl) ureidosulfonyl]-4-methanesulfonamidomethyl-benzoic acid)										
Mesotrione		104206-82-8	> 60000	11000	420000	180000	1900	9.8		
Metalaxyl		57837-19-1	65000	9100	14000	100	140000	92000		
Metaldehyde		108-62-3	34500		> 38830					
Metam sodium (degradate methyl isothiocyanate (MITC))		137-42-8	25.6		27.5	25	254	590		
Metam sodium and Metam potassium degradate-Methyl isothiocyanate (MITC)	2014	137-42-8	26.5		27.5	25	200	590		
Methamidophos		10265-92-6	12500	48.9	13	4.5	> 50000			
Methanearsonic Acid, disodium salt DSMA		144-21-8	> 56000		76500		1500	72700		
Methanearsonic Acid, sodium salt MSMA		2163-80-6	6650		38750		2800	53000		
Methidathion		950-37-8	1.1	6.3	1.5	0.66				
Methiocarb		2032-65-7	218	50	3.5	0.1				
Methomyl		16752-77-5	160	12	2.5	0.7				
Methoprene		40596-69-8	380	48	165	51				
Methoxychlor		72-43-5	7.5		0.7					

Methoxyfenoxide	2014	161050-58-4	> 2100	530	25	6.3	> 3400			
Methyl Bromide	2014	74-83-9	1950		1300		2200			
Methyl bromide degradate-bromide ion	2014		8E+06	7800	3E+06	7800	3E+06			
Methyl paraoxon		950-35-6			1.15	1				
Methyl parathion		298-00-0	925	< 10	0.485	0.25	15000	18000		
Metofluthrin	2014	240494-70-6	0.6		2.35					
Metribuzin		21087-64-9	21000	3000	2100	1290	8.7	130		
Metsulfuron		74223-64-6	> 75000	4500	> 75000		31	0.36		
Mevinphos	2013	7786-34-7								
Molinate		2212-67-1	105	390	170	340	220	3300		
MSMA	2014	2163-80-6	> 42500		38500		5630	104000		
Myclobutanil		88671-89-0	1200	980	5500		830			
Nabam	2013	142-59-6								
Naled		300-76-5	46	2.9	0.07	0.045	25	> 1800		
Napropamide		15299-99-7	3200	1100	7150	1100	3400			
Niclosamide	2014	50-65-7	15		17	56	41			
Nicosulfuron	2013	111991-09-4	> 500000		> 500000	43000				

Norflurazon		27314-13-2	4050	770	> 7500	1000	9.7	58.2		
Novaluron	2013	116714-46-6	> 490	6.16	0.075	0.03	3549	> 75.4		
Orthosulfamuron		213464-77-8	> 61000	6100	> 48650	6500	80	0.7		
Oryzalin		19044-88-3	1440	220	750	358	42	> 15.4		
Oxadiazon		19666-30-9	440	0.88	1090	30	5.2	41		
Oxamyl		23135-22-0	2100	770	90	27	120	30000		
Oxydemeon-Methyl	2014	301-12-2	365	5	95	46	> 100000			
Oxydemeton methyl		301-12-2	365	5	95	46	> 100000			
Oxyfluorfen		42874-03-3	101.5	1.3	40	13	0.29	0.35		
Oxypyrimidine (diazinon degradate)		4562-27-0	> 50500		> 51000		> 109000			
Oxytetracycline (hydrochloride salt)		2058-46-0	> 47450		> 51000					
Paclobutrazol	2014	76738-62-0	7950	49	120	9	40800	8		
Paraquat dichloride		1910-42-5	6000	< 369	600	< 36.9	0.396	71		
Pebulate		1114-71-2	3150		3315		230	1800		
Pendimethalin		40487-42-1	69	6.3	140	14.5	5.2	12.5		

Penoxsulam	2013	219714-96-2	> 51000	10200	> 49150	2950	92	3		
Pentachloroaniline (PCA)		527-20-8	28		150					
Pentachlorobenzene (PCB)		608-93-5	70		80					
Pentachloronitrobenzene (PCNB)		82-68-8	50	13	385	18				
Pentachlorophenol (PCP)		87-86-5	47.5		25					
Penthiopyrad	2013	183675-82-3	145	100	1265.5	471	1200	> 1205		
Permethrin		52645-53-1	0.395	0.0515	0.0106	0.0014	68			
Phorate		298-02-2	1.175	0.34	0.3	0.21	> 1300			
Phosmet	2014	732-11-6	35	3.2	1	0.8				
Phosphine										
Phthalimide (PI)	2014	133-07-3	19000		19500					
Picloram Acid		###### #	2750		17200		36900			
Picloram Potassium Salt		2545-60-0	6500	550	34150	11800				
Picloram TIPA Salt		6753-47-5	2E+05							
Picoxystrobin	2014	117428-22-5	32.5	36	12	1	4	210		
Pinoxaden		243973-20-8	10000				1200	4300		

Pinoxaden (NOA 447204)		.	> 60000		> 60000		95600	> 93500		
Pinoxaden (NOA 497854)		.	> 51500	> 960	> 50500	5800	> 100000	10000		
Piperalin		3478-94-2	385		945					
Piperonyl Butoxide		51-03-6	950	40	255	30				
Pirimicarb		23103-98-2	14500		9.5					
Pirimiphos Methyl		29232-93-7	202	180	55		1200			
Polybutene		9003-29-6								
Prallethrin		23031-36-9	6	3	3.1	0.65				
Prodiamine	2013	29091-21-2	> 6.5		> 6.5	1.5				
Profenofos		41198-08-7	7.05	2	0.465	0.2				
Prohexadione Calcium	2014	127277-53-6	> 47300		> 50000	12500	> 1100	> 1200		
Prometon	2014	1610-18-0	6000	19700	12850	3450	98			
Prometryn	2014	7287-19-6	1455	620	4850	1000	1.04	11.9		
Propachlor		1918-16-7	85		395		13.5			
Propanil		709-98-8	1150	9.1	600	86	16	110		

Propargite		2312-35-8	59	16	37	9	66.2	75000		
Propazine	2014	139-40-2	> 2190	560	> 2660	47	24.8	100		
Propetamphos		31218-83-4	94		1.65					
Propiconazole		60207-90-1	425	95	650	260	21	4828		
Propionic Acid		79-09-4	25500		11350					
Propoxur		114-26-1	1850		5.5					
Propylene Oxide	2014	75-56-9	42000		68500		> 860	> 870		
Propyzamide		23950-58-5	36000	7700	> 2800	600	> 4000	1180		
Pymetrozine	2014	123312-89-0	> 64000	11700	43500	25	17000	> 109000		
Pyraclostrobin		175013-18-0	3.1	2.35	7.85	4	1.5	1720		
Pyraflufen-ethyl	2013	129630-19-9	> 42.5	3.4	> 41	81	1.5	16		
Pyrasulfotole	2013	365400-11-9	> 48000	580	> 47900	12800	8300	28		
Pyrethrin		8003-34-7	2.55	1.9	5.8	0.86				
Pyridaben		96489-71-3	0.36	0.087	0.265	0.044	> 665	> 16.2		
Pyridalyl		179101-81-6	250	49	2.1	4.4				
Pyrifluquinazon	2014	337458-27-2	1950		1.4	< 1.4	3300			
Pyrifluquinazon degradate IV-01 (1,2,3,4-tetrahydro-3-	2014				0.7					

[(3-pyridylmethyl)amino]-6-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]quinazolin-2-one)										
Pyrifluquinazon degradate IV-02 (1,2,3,4-tetrahydro-3-[(3-pyridylmethyl)amino]-6-[1,2,2,2-tetrafluoro-1-(trifluoromethylene)ethyl]quinazolin-2-one)	2014				0.55					
Pyrifluquinazon degradate IV-203 (1,2,3,4-tetrahydro-6-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]quinazolin-2,4-dione)	2014				> 395					
Pyrifluquinazon degradate IV-28 (4-hydroxy-3-[(pyridine-3-ylmethylene)amino]-6-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-3-4-dihydro-1H-quinazolin-2-one)	2014				1.15					
Pyrimethanil		53112-28-0	5050	20	1500	1000	1800	7800		
Pyrimidinone	2014	67485-29-4	45		570					
Pyriproxyfen		95737-68-1	> 162.5	4.3	200	0.015	56	> 180		
Pyroxsulam		422556-08-9	> 43500	10100	> 49500	10400	111	2.57		
Quinclorac		84087-01-4	15800	16000	14900	110000	> 500	> 500		
Quizalofop ethyl		76578-14-8	230	11	1060		> 1770	> 82.8		

Resmethrin		10453-86-8	0.14	0.32	1.55					
Rimsulfuron		122931-48-0	> 195000		> 180000		> 29	11.6		
Rotenone		83-79-4	0.97	1.01	1.85	1.25				
Saflufenacil	2013	372137-35-4	> 54000	997	> 49000	1330	42	87		
Sethoxydim		74051-80-2	85000		39050			> 281		
Siduron		1982-49-6	4050	15	> 6850	6	212	212		
Simazine	2014	122-34-9	3200		500		2.24	140		
S-Metolachlor		87392-12-9	1600	30	550	1	8	21		
S-Metolachlor degradate ESA		.	24000		> 54000		> 99450	> 95100		
S-Metolachlor degradate OA		.	> 46550		7700		57100	> 95100		
Sodium Arsenite	2014	7784-46-5			2445	370				
Sodium chlorate		######	> 500000		460000	500000	133000	43000		
Sodium cyanide		143-33-9	94							
Sodium fluoroacetate		62-74-8	27000		175000					
Sodium Metabisulfite	2014	7681-57-4								
Sodium Tetrathiocarbonate		7345-69-9	3350		3300		17000			
Sodium tetrathiocarbonate		75-15-0	435		430		520			

degradate carbon disulfide										
Spinosad		168316-95-8	2970	498	7000	0.6	90	10600		
Spirodiclofen	2013	148477-71-8	> 17.55	1.95	> 22.75	11.1	> 60			
Spiromesifen	2013	283594-90-1	8.4	0.49	> 46.15	0.25	> 94	> 101.3		
Spiromesifen-enol	2013		> 51000	9200	> 50500					
Spirotetramat		203313-25-1	705	534	330	100	4050	4490		
Spirotetramat enol degradate		.	> 50000		37450		> 100000	5400		
Spirotetramat keto hydroxy degradate		.			> 50000					
Sulfentrazone		122836-35-5	46900	2950	30200	200	1.8	28.8		
Sulfometuron Methyl	2014	74222-97-2	> 74000		> 75000	97000	4.3	0.45		
Sulfosulfuron		141776-32-1	> 47500	100000	> 48000	102000	400	1		
Sulfoxaflor	2014	946578-00-3	> 181500	660	> 200000	50500	81200	> 99000		
Sulfoxaflor degradate- N-(methyl(oxido){1-[6-(trifluoromethyl) pyridin-3-yl]ethyl}-λ4-sulfanylidene) urea	2014		> 239000		> 102500					
Sulfur dioxide										
Sumithrin		26002-80-2	7.9	1.1	2.2	0.47				

Tau-Fluvalinate		102851-06-9	0.175		0.47	0.1				
Tebuconazole		107534-96-3	1135	12	1440	120	1450	151.5		
Tebufenozide		112410-23-8	1500	< 48	1900	4.3	> 740			
Tebupirimphos		96182-53-5	44.5	130	0.039	0.011	630	8800		
Tebuthiuron		34014-18-1	53000	9300	148500	21800	50	135		
Tefluthrin	2013	79538-32-2	0.03	0.004	0.035	0.008				
Telone		542-75-6	540		45	70	7900	20000		
Tembotrione	2013	335104-84-2	> 50000	604	24450	5100	310	5.2		
Temephos		3383-96-8	1745		5					
Terbacil		5902-51-2	23100	1200	32500	640	11	140		
Terbufos		13071-79-9	0.385	0.64	0.1	0.03				
Terbuthylazine		5915-41-3	1700		25450					
Tetrachlorvinphos		961-11-5	265		0.95		510			
Tetraconazole	2013	112281-77-3	1925	300	1315	190		310		
Tetramethrin		7696-12-0	1.85		22.5					
TFM (3-Trifluoromethyl-4-nitrophenol)	2013	88-30-2	300		1900		1200			

Thiacloprid	2013	111988-49-9	12600	918	18.9	0.97	45000	> 95400		
Thiacloprid amide	2013		> 39300		15600	100				
Thiacloprid sulfonic acid	2013		> 47550		> 48050		> 100000			
Thiamethoxam		153719-23-4	> 50000	20000	17.5		> 97000	> 90000		
Thiencarbazone-methyl		317815-83-1	> 52000	4800	> 47000	3540	298	0.8		
Thiobencarb		28249-77-6	280		50	1	17	770		
Thiodicarb		59669-26-0	605	25	2.65	9	> 8300			
Thiophanate methyl		23564-05-8	4150	2	2700	3	930	> 4700		
Thiram		137-26-8	21	530	105	170.6	140	1600		
Tolclofos-methyl	2014	57018-04-9	345	< 12	350	26	780			
Tolclofos-methyl degradate- O-methyl O-(2,6-dichloro-4-methylphenyl)hydrogen phosphorothioate(DM-TM)	2014		> 55000		> 47500		> 97000			
Topramezone	2014	210631-68-8	> 14190	2930	14850	48600	19000	6.7		
Topramezone primary degradate (M670H05)	2014		52650		> 50000			360		
Tralkoxydim		87820-88-0	> 3750		> 87000	2100	7700	2600		

Tralomethrin		66841-25-6	0.8	0.088	0.0195	0.0044				
Triadimefon	2013	43121-43-3	2050	41	800	52	17000			
Triallate		2303-17-5	600	38	45.5	13	120	2400		
Triasulfuron		82097-50-5	> 50000	68600	> 50000	105000				
Triazine DACT degradate		.	> 50000		> 50000					
Triazine DEA degradate		.					1000			
Triazine DIA degradate		.	8500		63000		2500			
Triazine HA degradate		2163-68-0	> 1500		> 2050		> 10000			
Tribenuron methyl	2013	101200-48-0	> 50000	11800	360000	< 28000	22	2		
Tribufos		78-48-8	122.5	3.5	3.4	1.56	148	1100		
Trichlorfon		52-68-6	79	110	2.65	0.0057				
Triclopyr acid		55335-06-3	58500		66450		29800			
Triclopyr butoxyethyl ester (BEE)		64700-56-7	130	19	125		70	860		
Triclopyr degradate (TCP)		55335-06-3	950		6700		2300			
Triclopyr triethylamine (TEA)		57213-69-1	39600	> 32200	173000	25000	4100	6100		
Trifloxystrobin	2014	141517-21-7	7.15	4.3	12.65	2.76	37.1	> 1930		

Trifloxystrobin degradate CGA-321113	2014	141517-21-7	> 53000		> 47650	3200	77100			
Trifloxysulfuron-Sodium (CGA-362622)	2014	290332-10-4	> 51500	9520	> 54000	549	6.5	0.24		
Trifloxysulfuron-Sodium degradate- CGA 382997	2014		> 48350		> 49750		> 95850			
Trifloxysulfuron-Sodium degradate- CGA-368732	2014		> 52000		> 59500		23000			
Triflumizole		68694-11-1	290	33	700	67	140	720		
Trifluralin		1582-09-8	20.5	1.14	280	2.4	7.52	43.5		
Trinexapac-ethyl	2014	95266-40-3	17500	410	> 72750	2400	350	190		
Triphenyltin Hydroxide (TPTH)	2014	76-87-9	3.55	0.065	5	< 0.2	14	8.3		
Urea sulfate		21351-39-3	40000				11500			
Vinclozolin		50471-44-8	1420	60	2000	790	< 1060	> 900		
Zeta-cypermetherin		52315-07-8	0.195	0.14	0.0018	0.00059				
Zinc Phosphide		1314-84-7								
Ziram		137-30-4	4.85	101	24	39	67	370		
Zoxamide		156052-68-5	78	3.48	> 390	39	10	19		

Footnotes

- [1] Benchmark = Toxicity value x LOC. For acute fish, toxicity value is generally the lowest 96-hour LC50 in a standardized test (usually with rainbow trout, fathead minnow, or bluegill), and the LOC is 0.5.
- [2] Benchmark = Toxicity value x LOC. For chronic fish, toxicity value is usually the lowest NOEAC from a life-cycle or early life stage test (usually with rainbow trout or fathead minnow), and the LOC is 1.
- [3] Benchmark = Toxicity value x LOC. For acute invertebrate, toxicity value is usually the lowest 48- or 96-hour EC_{50} or LC_{50} in a standardized test (usually with midge, scud, or daphnids), and the LOC is 0.5.
- [4] Benchmark = Toxicity value x LOC. For chronic invertebrates, toxicity value is usually the lowest NOAEC from a life-cycle test with invertebrates (usually with midge, scud, or daphnids), and the LOC is 1.
- [5] Benchmark = Toxicity value x LOC. For acute nonvascular plants, toxicity value is usually a short-term (less than 10 days) EC_{50} (usually with green algae or diatoms), and the LOC is 1.
- [6] Benchmark = Toxicity value x LOC. For acute vascular plants, toxicity value is usually a short-term (less than 10 days) EC50 (usually with duckweed) and the LOC is 1.
- [7] An acute-to-chronic ratio was used to calculate the chronic endpoint and benchmark, which may underestimate chronic toxicity.
- [8] Although the underlying acute toxicity value is greater than or equal to the chronic toxicity value, the acute benchmark is lower than the chronic benchmark because acute and chronic toxicity values were multiplied by LOC values of 0.5 and 1, respectively.
- [9] Original toxicity values are in micrograms of acid equivalents per liter. For 2,4-D and 2,4-DB, the toxicity values selected were the lowest available values for the acid or salt forms. For MCPA, acute toxicity values were the lowest for the acid, salt or ester forms, and chronic toxicity values were the lowest of the acid and salt forms. For Dicamba the toxicity values were the lowest of the acid or salt forms. (Selection was consistent with risk quotients in the cited USEPA references.)
- [10] The acute toxicity values were the lowest of the acid, salt or ester forms, and the chronic toxicity values were the lowest of the acid and salt forms of triclopyr. (Selection was consistent with risk quotients in the cited USEPA reference.)
- [11] Toxicity values and benchmarks apply to permethrin. If monitoring data represent only the *cis* isomer of permethrin in water, comparison with benchmarks may underestimate potential toxicity.

Appendix B

Surface Water Ambient Monitoring Program

Field Sample Form

SWAMP Field Data Sheet (Water Chemistry & Discrete Probe) - EventType=WQ

Entered in d-base (initial/date) | Pg of Pgs

*StationID: ___ ___ ___ ___ ___ ___ ___ ___ ___ ___ | *Date (mm/dd/yyyy): / / | *Group: | *Agency:

*Funding: ___ ___ ___ ___ ___ ___ ___ ___ | ArrivalTime: | DepartureTime: | *SampleTime (1st sample): | *Protocol:

*ProjectCode: | *Personnel: | *Purpose (circle applicable): WaterChem WaterTox Habitat FieldMeas | *PurposeFailure:

*Location: Bank Thalweg Midchannel OpenWater | *GPS/DGPS | Lat (dd.ddddd) | Long (ddd.ddddd) | OCCUPATION METHOD: Walk-in Bridge R/V _____ Other

GPS Device: | Target: | - | STARTING BANK (facing downstream): LB / RB / NA

Datum: NAD83 | Accuracy (ft / m): | *Actual: | - | Point of Sample (if Integrated, then -88 in dbase)

Habitat Observations (CollectionMethod = Habitat_generic)

WADEABILITY: Y / N / Unk | BEAUFORT SCALE (see attachment): | DISTANCE FROM BANK (m): | STREAM WIDTH (m): | WATER DEPTH (m):

SITE ODOR: None,Sulfides,Sewage,Petroleum,Smoke,Other_____

SKY CODE: Clear, Partly Cloudy, Overcast, Fog, Smoky, Hazy

WIND DIRECTION (from): 

HYDROMODIFICATION: None, Bridge, Pipes, ConcreteChannel, GradeControl, Culvert, AerialZipline, Other LOCATION (to sample): US / DS / WI / NA

OTHER PRESENCE: Vascular,Nonvascular,OilySheen,Foam,Trash,Other_____

PHOTOS (RB & LB assigned when facing downstream; RENAME to StationCode_yyyy_mm_dd_uniquecode): 1: (RB / LB / BB / US / DS / ##)

DOMINANT SUBSTRATE: Bedrock, Concrete, Cobble, Boulder, Gravel, Sand, Mud, Unk, Other_____

WATERCLARITY: Clear (see bottom), Cloudy (>4" vis), Murky (<4" vis) | PRECIPITATION: None, Fog, Drizzle, Rain, Snow | 2: (RB / LB / BB / US / DS / ##)

WATERODOR: None, Sulfides, Sewage, Petroleum, Mixed, Other_____ | PRECIPITATION (last 24 hrs): Unknown, <1", >1", None

WATERCOLOR: Colorless, Green, Yellow, Brown | EVIDENCE OF FIRES: No, <1 year, <5 years | 3: (RB / LB / BB / US / DS / ##)

OVERLAND RUNOFF (Last 24 hrs): none, light, moderate / heavy, unknown

OBSERVED FLOW: NA, Dry Waterbody Bed, No Obs Flow, Isolated Pool, Trickle (<0.1cfs), 0.1-1cfs, 1-5cfs, 5-20cfs, 20-50cfs, 50-200cfs, >200cfs

Field Measurements (SampleType = FieldMeasure; Method = Field)

	DepthCollec (m)	Velocity (fps)	Air Temp (°C)	Water Temp (°C)	pH	O_2 (mg/L)	O_2 (%)	Specific Conductivity (uS/cm)	Salinity (ppt)	Turbidity (ntu)			
SUBSURF/MID/ BOTTOM/REP													
SUBSURF/MID/ BOTTOM/REP													
SUBSURF/MID/ BOTTOM/REP													
Instrument:													
Calib. Date:													

Samples Taken (# of containers filled) - Method=Water_Grab

Field Dup YES / NO: (SampleType = Grab / Integrated; LABEL_ID = FieldQA; create collection record upon data entry

SAMPLE TYPE: Grab / Integrated | COLLECTION DEVICE: Indiv bottle (by hand, by pole, by bucket); Teflon tubing; Kemmer; Pole & Beaker; Other _____

	DepthCollec (m)	Inorganics	Bacteria	Chl a	TSS / SSC	TOC / DOC	Total Hg	Dissolved Mercury	Total Metals	Dissolved Metals	Organics	Toxicity	VOAs
Sub/Surface													
Sub/Surface													

COMMENTS:

TOXICITY TESTING

Toxicity test results will be available for this sample

- ☐ Yes
- ☐ No

Water (check all that apply):

- ☐ *Pimephales promelas*
- ☐ *Ceriodaphnia dubia*
- ☐ *Selenastrum capricornutum*
- ☐ *Hyalella azteca*
- ☐ Other: _____

Sediment (check all that apply):

- ☐ *Hyalella azteca*
- ☐ Other: _____

Sample information for water/sediment sample sent to lab for toxicity testing

Site name: _____

Sample #: _____

Sample collection date: _____

Sample collection time: _____

Lab conducting analysis: _____

Database through which data will be made available: _____

Appendix C

ORCL
Pesticide Fate and Research Group

Laboratory Analysis Filter Form

LABORATORY ANALYSIS FILTER FORM

Field ID _____

Lab ID _____

Corresponding WS#:_____

Study Name _____ **Site Name** _____

Date _____ **Time** _____

Sample Type: ☐ ENV ☐ Replicate #_____ ☐ Blank

☐ Lab Matrix Spike ☐ Field Matrix Spike ☐ Matrix Spike Replicate # _____

EXTRACTION INFORMATION

Extraction method*:* ☐ Sonication ☐ Other_____

Date extracted _____ **Person extracting** _____

Foil wt (g): _____

Foil & Filter wt (g): _____

Foil, Filter & Sediment wt (g): _____

Surrogate (#,vol)_____

Matrix spike (#,vol) _____

Comments: _____

_____

ELUTION AND ANALYSIS INFORMATION

Date of Carbon:Alumina (if applicable): _____ **Person Eluting:** _____

ISTD # _____ **ISTD Volume**_____

Analytical method: ☐ GC/MS ☐ GC/MS/MS ☐ LC/MS/MS

Date Run _____ **Date Rerun (if any)** _____

Comments: _____

Entered into Sample Tracking Database: Date: _____ **Initials:** _____

Appendix D

ORCL
Pesticide Fate and Research Group

Laboratory Analysis Water Form

LABORATORY ANALYSIS WATER FORM

Field ID _____

Lab ID_____ _____

Study Name_____ **Site Name**_____

Date_____**Time**_____

Sample Type: ☐ ENV ☐ Replicate #___ ☐ Lab Matrix spike ☐ Field Matrix Spike

☐ Matrix Spike Replicate#___

☐ Lab Blank ☐ Field Blank ☐ NWQL Sample

EXTRACTION INFORMATION

Extraction Method: ☐ HLB ☐ Liquid/Liquid ☐ Bottle Wash

☐ Other _____

Date Extracted _____ **Volume Extracted**_____(mL)**Person Extracting**_____

Surrogate (#, vol) _____

Matrix spike (#, vol)_____

Comments:_____

_____

ELUTION AND ANALYSIS INFORMATION

Date Eluted _____ **Person Eluting** _____**ISTD (#, vol)** _____

Analytical method: ☐ GC/MS ☐ GC/MS/MS ☐ LC/MS/MS

Date Run_____ **Date Rerun (if any)**_____

Comments:_____

_____

Entered into Sample Tracking Database:Date:_____ **Initials:**_____

Appendix E

ORCL
Pesticide Fate and Research Group

Standard Operating Procedure
for Water Filtering

Pesticide Fate Research Group

FILTERING

All samples that will be extracted onto SPE cartridges should be filtered using the following method. Samples that will be extracted via liquid-liquid method may or may not be filtered. Check the study procedures for that sample.

WHAT YOU NEED

Filter setup and peristaltic pump
0.7 um borosilicate (glass) fiber filters, baked and wrapped in foil
Forceps
Clean, baked, 1 liter, clear glass graduated bottles
1 liter bottle of methanol
1 liter bottle of DI organic free water
Wide-mouth, plastic methanol waste bottle
Teflon methanol squirt bottle
Teflon DI organic free water squirt bottle
Plastic beaker
Sample field forms

PROCEDURE

Label a 1L clear glass graduated bottle with sample information such as date, location, time and type of sample. This information can be found on the field form or on the sample bottle itself. If there is no field form, one must be filled out using the information form the label on the sample bottle

Clean the filtering apparatus, without a fiber filter in place, by pumping 100 mL of methanol into methanol waste bottle, followed by 500 mL DI organic free water into plastic beaker (to be poured down sink).

Open filter setup and place fiber filter carefully in place using forceps (DO NOT TOUCH FILTER WITH YOUR HANDS). Close filter and tighten clamp with hand. Open pressure valve at the top of the filter apparatus. Start pumping sample through filter allowing the first 50 mL or so to go into plastic beaker or down the drain.. The pressure valve at the top of the filter apparatus is left open until water starts squirting out, then it is closed immediately. Collect just over 1L of filtered sample in the labeled bottle.

When finished, open filter setup, remove used filter with forceps and discard. Using a squirt bottle filled with organic free water, squirt off any filter residues and close filter apparatus.

Clean the filter setup, without fiber filter in place, by pumping through 100 to 200 mL methanol into methanol waste bottle, followed by 500 to 800 mL organic free water into plastic beaker or down drain. Continue on to next sample or if finished, wrap ends of tubing in foil and crimp.

Continue on to Extraction Procedure.

This page was last updated May 22, 2008
If you have any questions or comments about this document contact:
Kelly Smalling (ksmall@usgs.gov)

Appendix F

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Pesticide Fate Research Group

Standard Operating Procedure for
Suspended Sediment on Filter Paper Extraction
for GCMS Analysis

Pesticide Fate Research Group

Suspended sediment on Filter Paper EXTRACTION for GCMS analysis

1. Prior to filtering (see filtering SOP for filtering procedure) weigh a piece of clean foil large enough to envelope the filter for storage and the weight of the filter+foil. Record values on lab form.
2. After filtering, carefully remove the filter with its trapped suspended sediment from the filter plate and place it on top of the foil corresponding to its lab form.
3. Allow the filter to air dry under a tent of foil. Once dry fold the filter in half with clean tweezers and enclose in its foil. Weigh and record the foil+filter+sediment weight on the lab form.
4. Either extract immediately or store in freezer.

Extraction:

1. Using a clean set of forceps and scissors that have been rinsed with acetone followed by DCM, cut the foil so that it will fit into a 250 mL Erlenmeyer flask.
2. Add 50 uL of sediment surrogate directly to the filter with a microsyringe (in addition add 50 uL of pesticide spike if applicable) and pour a mixture of 1:1 DCM/Acetone into the Erlenmeyer, enough to submerge it (~50-75 mL). Cover with foil.
3. Sonicate for 15 minutes then decant into a tubrovap tube through a funnel containing a small amount of sodium sulfate and glass wool. Rinse the sodium sulfate with DCM.
4. Refill the Erlenmeyer with 1:1 DCM/Acetone mixture again until top of filters are submerged (~50 mL)
5. Cover with foil & sonicate for 15 min.
6. Decant again into the same turbovap collection tube.
7. Rinse Erlenmeyer with DCM 2x & pour through funnel
8. Rinse Na_2SO_4 with DCM
9. Blow down in turbovap to approximately 0.5 mL
10. Perform carbon alumina if clean-up is necessary
11. Transfer sample to concentrator tube
12. Blow down to 0.5 mL
13. Exchange 2x
    a. Add EtOAc (ethyl acetate) to bring volume up to 1 mL & gently swirl
    b. Blow down to 0.5 mL again
    c. Add EtOAc to bring volume up to 1 mL & swirl
14. Blow down to 200 uL on N-Evap.
15. Add 20 µL IS (internal standard) & put in labeled GCMS vial. Store in freezer

Appendix G

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Pesticide Fate Research Group

Water Extraction for GCMS Analysis
Using HLB Cartridges

Pesticide Fate Research Group

WATER EXTRACTION for GCMS analysis using HLB cartridges

1. Fill out a Laboratory Analysis form for each filtered sample. Each form includes field information such as date, time, site information and sample type and assigns the sample its own unique sample identification number. This form will be used to document all laboratory work done on the sample.

2. Measure 1000 mL (1 liter) of sample with a clean one-liter graduated cylinder. If the volume of sample is less than 1000 mL, measure the volume accurately. ALWAYS record sample volume on laboratory analysis form.

3. Remove water surrogate from freezer allowing it to warm to room temperature. This step is very important to measure the correct volume (you can also warm the vial quickly in your hands, if needed). Slowly pull up 50 µL of the surrogate with a microsyringe and then gently wipe the outer surface of the needle. Add the surrogate to the sample by placing the tip under the water surface and slowly expelling the surrogate into the sample. Shake the sample well. If sample is a matrix spike, add 50 µL of matrix spike (if more than one spike, add 50 µL of each matrix spike) to sample using a microsyringe in the manner described above and shake well.

4. Before use, the solid phase extraction (SPE) HLB cartridges must be clean. Using a manifold, allow two column volumes of ethyl acetate to gravity drip through cartridge followed by two column volumes of methanol and then by one column volume of organic free water making sure that some water is left above the frit (a few cm of water above the frit).

5. Label cartridge with blue tape to signify it is a GCMS water sample. The label should contain the project and lab identification number (WS#).

6. Vacuum manifold should be clean prior to use (if not previously cleaned) by pumping through 25-50 mL of methanol (methanol waste collected in methanol waste container) followed by 200-500 mL of organic-free water.

7. Attach the cartridge to the vacuum manifold and begin to draw the sample through cartridge at a flow rate of 10 mL per minute. Measure the flow rate with a small graduated cylinder several times during the extraction. Just a tip, make sure cartridge is full of organic-free water before attaching to pump. And also make sure there is organic-free water in the tubing rather than air before the pumping is started so as not to push air through the cartridge. Keep an eye on the extraction as sometimes the SPE cartridge clogs, if the cartridge becomes clogged and the sample will not pump through, you will need to use another cartridge for the sample.

8. Once the extraction is complete, remove the tubing and vacuum pump out any remaining water. Then further dry with CO_2 on the manifold equipped with a timer. After drying for an hour, either immediately elute the cartridge or put it in a ziplock bag and place in the freezer for storage.

9. Include any important comments, such as added surrogate twice, lost some sample when extracting etc. on the laboratory analysis form. THERE IS NO SUCH THING AS UNNECESSARY INFORMATION!

10. Bottle rinse: add sodium sulfate to the empty glass bottle to remove any residual water. Add approximately 4 mL of methylene chloride, cap the bottle and gently roll the solvent around the bottle. Empty the solvent into a concentrator tube and repeat methylene chloride rinse two more times. Using the N-evap, reduce the methylene chloride fraction to ~0.5-1 mL.

11. To elute the sample put the cartridge on the manifold (be sure the cartridge is at room temperature if it had been stored in the freezer). Elute with 12 mL of ethyl acetate, collect the ethyl acetate in the concentrator tube containing its associated bottle rinse. Then blow down the sample to 200 µL and add 20 µL of internal standard. Transfer sample to GCMS vial labeled with its project and lab identification number.

12. Remember to clean the pumps by pumping through 25-50 mL of methanol followed by 200-500 mL of organic-free water.

Appendix H

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Pesticide Fate Research Group

Water Extraction for LCMSMS Analysis
Using HLB Cartridges

Pesticide Fate Research Group

WATER EXTRACTION for LCMSMS analysis using HLB cartridges

1. Fill out a Laboratory Analysis form for each filtered sample.

2. Measure 1000 mL (1 liter) of sample with a clean one-liter graduated cylinder. If the volume of sample is less than 1000 mL, measure the volume accurately. To clean the graduated cylinder, rinse with organic-free water (to remove any remaining sediment particles, rinse sparingly with methanol, and finish with three rinses of organic-free water. ALWAYS record sample volume on laboratory analysis form.

3. Remove water surrogate, (1ng/uL D4-imidacloprid, monuron in ACN) from freezer allowing it to warm to room temperature. This step is very important to measure the correct volume (you can also warm the vial quickly in your hands, if needed). Slowly pull up 100 µL of the surrogate with a microsyringe and then gently wipe the outer surface of the needle. Add the surrogate to the sample by placing the tip under the water surface and slowly expelling the surrogate into the sample. Shake the sample well. If sample is a matrix spike, add 100 µL of matrix spike (if more than one spike, add 100 µL of each matrix spike) to sample using a microsyringe in the manner described above and shake well.

4. Before use, the solid phase extraction (SPE) HLB cartridges must be clean. Using a manifold, allow one column volume of dichloromethane to gravity drip through cartridge followed by one column volume of acetone and then by one column volume of organic free water making sure that some water is left above the frit (a few cm of water above the frit).

5. Label cartridge with purple tape to signify it is a LCMSMS water sample. Include project and the correct water sample ID.

6. Vacumm manifold tubes should be clean prior to use (if not previously cleaned) by pumping through 10-15 mL of methanol (methanol waste collected in methanol waste container) followed by 20-50 mL of organic-free water.

7. Attach the cartridge to the vacuum manifold and begin to draw the sample through cartridge at a flow rate of 10 mL per minute. Measure the flow rate with a small graduated cylinder several times during the extraction. Just a tip, make sure cartridge is full of organic-free water before attaching to pump. And also make sure there is organic-free water in the tubing rather than air before the pumping is started so as not to push air through the cartridge. Keep an eye on the extraction as sometimes the SPE cartridge clogs, if the cartridge becomes clogged and the sample will not pump through, you will need to use another cartridge for the sample.

8. Once the extraction is complete, the cartridges are dried by placing the cartridge of the manifold and vacuum pumping any remaining water. The cartridges are then further dried with CO_2 using the manifold and timer. After drying for an hour, the cartridges are either immediately eluted or put in a ziplock bag with a label (date or study or other pertinent information) and placed in the freezer for storage.

9. Include any important comments, such as added surrogate twice, lost some sample when extracting etc. on the laboratory analysis form. THERE IS NO SUCH THING AS UNNECESSARY INFORMATION!

10. To elute the sample put the cartridge on the manifold (be sure the cartridge is at room temperature if it had been stored in the freezer). Elute with 10 mL of 1:1 dichloromethane:acetone, in a concentrator tube. Using the N-evap gently blow the sample down to a 0.5 mL, add 0.5 mL acetonitrile and blow down to ~180 µL. Add 20 µL of 5 ng/µL internal standard (13C caffeine in ACN) and transfer sample to GCMS vial.

11. Remember to clean the pumps by pumping through 25-50 mL of methanol followed by 200-500 mL of organic-free water.

This page was last updated January 30, 2015
If you have any questions or comments about this document contact: Michelle Hladik

Appendix I

Chain of Custody

CHAIN OF CUSTODY

REGIONAL WATER QUALITY CONTROL BOARD
CENTRAL VALLEY REGION
11020 Sun Center Dr. #200
Rancho Cordova, CA 95670
PHONE: (916) 464-3291
FAX:(916) 464-3291

MAIL SAMPLES TO:
Pesticide Fate Research Lab
USGS California Water Science Center
6000 J Street
Sacramento, CA 95819

PROJECT NAME: Coordinated Pesticide Reconnaissance Study

Contact Name and Number: Jim Orlando, USGS Office 916-278-3271 Cell 530-218-7198 jorlando@usgs.gov
Melissa Dekar, CVRWQCB Office: 916-464-4603 melissa.dekar@waterboards.ca.gov

SAMPLER (signature)	**PRINT NAME**	**SAMPLER PHONE NUMBER**

SAMPLE					**MATRIX**				**ANALYSIS REQUESTED**		**LAB NO.**
Site ID	**Date**	**Time**	**No.**	**Container type**		**Composite**	**Grab**	**Preserved**	Pesticide Scan - LCMSMS	Pesticide Scan -GCMS	

RELINQUISHED BY (Signature)	**RECEIVED BY (Signature)**	**RELINQUISHED BY (Signature)**	**RECEIVED BY (Signature)**
DATE/TIME		**DATE/TIME**	
RELINQUISHED BY (Signature)	**RECEIVED BY (Signature)**	**RELINQUISHED BY (Signature)**	**RECEIVED BY (Signature)**
DATE/TIME		**DATE/TIME**	

Appendix J

SWAMP Measurement Quality Objectives

http://www.waterboards.ca.gov/water_issues/programs/swamp/docs/mqo/ 6_syn_water.pdf

Synthetic Organic Compounds in Fresh and Marine Water

Groups associated with this category are defined in the following compound lists:

Carbamate Pesticides	Organotins	Pyrethroid Pesticides
Diesel Range Organics	Polynuclear Aromatic Hydrocarbons	Surfactants
Glyphosates	Polybrominated Diphenyl Ethers	Triazine Pesticides
Organochlorine Pesticides	Polychlorinated Biphenyls	Wastewater Organochlorine Pesticides
Organophosphate Pesticides	Phenols	

Terms appearing in the tables are defined in the *Surface Water Ambient Monitoring Program Quality Assurance Program Plan*, which contains a glossary (Appendix E), as well as a list of abbreviations and acronyms (Appendix F).

Table 1: Quality Control[1, 2]: Synthetic Organic Compounds in Fresh and Marine Water[3]

Laboratory Quality Control	Frequency of Analysis	Measurement Quality Objective
Tuning[4]	Per analytical method	Per analytical method
Calibration	Initial method setup or when the calibration verification fails	• Correlation coefficient (r^2 >0.990) for linear and non-linear curves • If RSD<15%, average RF may be used to quantitate; otherwise use equation of the curve • First- or second-order curves only (not forced through the origin) • Refer to SW-846 methods for SPCC and CCC criteria[4] • Minimum of 5 points per curve (one of them at or below the RL)
Calibration Verification	Per 12 hours	• Expected response or expected concentration ±20% • RF for SPCCs=initial calibration[4]
Laboratory Blank	Per 20 samples or per analytical batch, whichever is more frequent	<RL for target analytes
Reference Material	Per 20 samples or per analytical batch (preferably blind)	70-130% recovery if certified; otherwise, 50-150% recovery
Matrix Spike	Per 20 samples or per analytical batch, whichever is more frequent	50-150% or based on historical laboratory control limits (average±3SD)
Matrix Spike Duplicate	Per 20 samples or per analytical batch, whichever is more frequent	50-150% or based on historical laboratory control limits (average±3SD); RPD<25%
Surrogate	Included in all samples and all QC samples	Based on historical laboratory control limits (50-150% or better)
Internal Standard	Included in all samples and all QC samples (as available)	Per laboratory procedure

Table 1: Quality Control[1, 2]: Synthetic Organic Compounds in Fresh and Marine Water[3] (continued)

Field Quality Control	Frequency of Analysis	Measurement Quality Objective
Field Duplicate	5% of total project sample count	Per method
Field Blank, Travel Blank, Equipment Blank	Per method	<RL for target analytes

[1] Unless method specifies more stringent requirements; ELISA results must be assessed against kit requirements.

[2] Pyrethroids quality control guidelines are presented in Table 2 immediately below.

[3] All detected analytes must be confirmed with a second column, second technique, or mass spectrometry.

[4] Mass spectrometry only

USEPA SUFFICIENTLY SENSITIVE METHODS RULE

Dania Jimmerson, Central Valley Regional Water Quality Control Board

Agenda Item #11

Sufficiently Sensitive Methods Rule (SSM Rule)

Dania Jimmerson

Implementing SSM Rule NPDES Permits

- NPDES Permits
  - POTWs
  - Groundwater Cleanup Sites
  - Aquaculture Facilities
  - Dewatering for Construction Sites
- Regional Water Quality Control Board, Central Valley
  - Redding, Sacramento, and Fresno

Purpose of SSM Rule

The purpose of this rulemaking is to clarify that NPDES applicants and permittees must use EPA-approved analytical methods that are capable of detecting and measuring the pollutants at, or below, the applicable water quality criteria and permit limits.

BACKGROUND

- NPDES Permits
  - 40 CFR 136 – EPA Approved Methods
- Outdated: SIP Minimum Levels (MLs)
  - Reporting Limits (RLs) equal to or less than the SIP MLs
- SSM Rule
  - Effective: 18 September 2015

OBJECTIVE

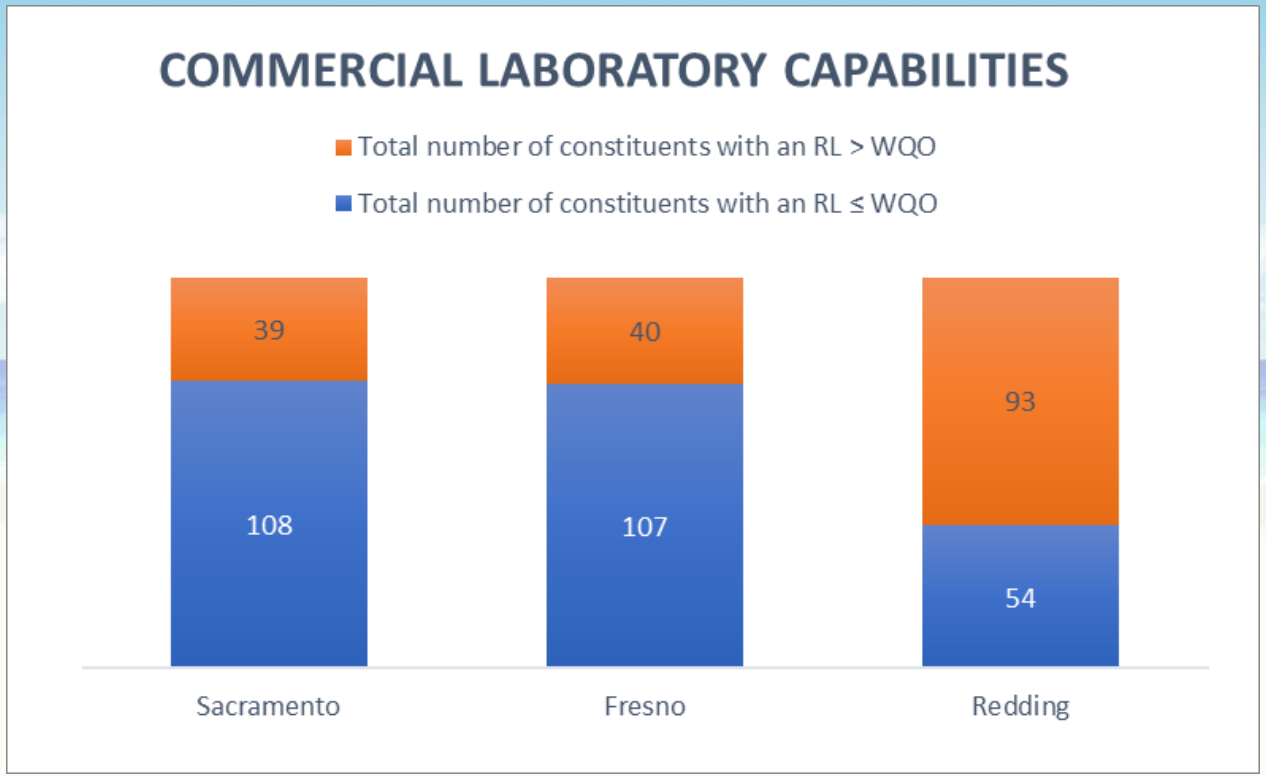
Share information regarding our proposed implementation of the SSM Rule and how it may impact dischargers and/or laboratories.

Regionwide Laboratory Survey

- Why?
  - RB Staff needed to know current capabilities
  - Cannot determine compliance without a “baseline”
- Determine how many constituents with RL > WQO
- Results…

RL vs. WQO

Determining if the chosen RL is lowest available



Proposed NPDES Attachment

No	Category	CTR #	Category - Parameter/Constituent	Cas Number	Units	Effluent Sample Type	WQO	Reference	Project Specific MDL	Project Specific RL	Project Specific Analytical Method
			VIII. NUTRIENTS								
1		7	Ammonia (as N)	7664-41-7	mg/L	24-hr composite	1.5	MUN			
2		8	Nitrate (as N)	14797-55-8	mg/L	24-hr composite	10	Primary MCL			
3		9	Nitrite (as N)	14797-65-0	mg/L	24-hr composite	1	Primary MCL			
	Category		***IX. OTHER CONSTITUENTS OF CONCERN***								
1	A		1,2,3-Trichloropropane (TCP)	96-18-4	ug/L	Grab	0.005	Drinking Water Notification Level			
2			Acetone	67-64-1	µg/L	Grab	--	--			
3	B		Carbon Disulfide	75-15-0	µg/L	Grab	160	Drinking Water Notification Level			
4			Stoddard Solvent	8052-41-3	µg/L	Grab	--	--			
5			Trichlorofluoromethane	75-69-4	µg/L	Grab	150	Primary MCL			
6			1,1,2-Trichloro-1,2,2-Trifluoroethane	76-13-1	µg/L	Grab	1200	Primary MCL			
7			Styrene	100-42-5	µg/L	Grab	100	Primary MCL			
8			Xylenes	1330-20-7	µg/L	Grab	1750	Primary MCL			
9	C		Barium	7440-39-3	µg/L	24-hr composite	1000	Primary MCL			
10			Fluoride	16984-48-8	mg/L	24-hr composite	2	Primary MCL			
11			Molybdenum	7439-98-7	µg/L	24-hr composite	10	Ag WQG			
12			Tributyltin	688-73-3	µg/L	24-hr composite	--	--			
13			Alachlor	15972-60-8	µg/L	24-hr composite	2	Primary MCL			
14			Atrazine	1912-24-9	µg/L	24-hr composite	1	Primary MCL			
15			Bentazon	25057-89-0	µg/L	24-hr composite	18	Primary MCL			

RB5 Proposed Process

When RLs > WQO and/or effluent limit

- Laboratory Survey Information
- WQOs and lowest RLs (survey)
  - Assists staff in determining available RLs that comply with the SSM Rule.
- RLs will need to be updated periodically
  - To ensure the lowest available RLs are being used.

RB5 Proposed Process

When RLs > WQO and/or effluent limit

- RB5 collaborating with ELAP to determine:
  - Collect updated information regarding laboratory capabilities
- Notify laboratories about changes RLs
  - WQOs ➔ Proposed NPDES Attachment
- As laboratories obtain competitive RLs
  - Cost of Compliance
  - Holding time

} Less of a concern

Potential Issues Identified

- Current laboratory capabilities
  - Vary lab to lab
  - Some will not have RLs at or below the WQO, some will
  - Future lab capabilities, remain competitive
- Laboratories able to meet sufficiently sensitive RLs
  - Sample demand
  - Holding times
  - Remote
  - Not using local labs
- Contractor Procurement
  - Funding limitations

DIVISION OF DRINKING WATER UPDATES

Melissa Hall, Division of Drinking Water
Agenda Item #12

CLOSE – REVIEW ACTION ITEMS

Stephen Clark, Chairperson

Agenda Item #13

ADJOURN