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Study 334. Effects of sampling frequency on storm water runoff pesticide characterization

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1. Problem Statement

Surface water monitoring is an integral component of the California Department of Pesticide Regulation (CDPR) program to assess the potential impacts of urban and agricultural pesticide uses on California's aquatic environments. California is the largest user of pesticides in the United States (Meeling, 2019). More than two hundred million pounds of reported pesticide active ingredients (AIs) were applied statewide during 2018 (CDPR, 2020). Pesticide concentrations measured in California waterbodies frequently exceed their associated lowest acute or chronic aquatic life benchmarks which are calculated by the U.S. Environmental Protection Agency (US EPA) (Burant, 2021; Ensminger, 2021; Main, 2020; Wagner, 2020). This high frequency of pesticide detection and benchmark exceedance in California surface waters indicates the potential for pesticide runoff to adversely impact non-target aquatic organisms and communities.

Storm runoff has the potential to transport residual pesticides from the site of application to adjacent non-target waterways. High energy storm flow can reduce the time available for natural reactions such as sorption or degradation, thereby increasing the transfer of pesticides from soil and plant surfaces into surface waters (Müller et al., 2003). Timing of peak pesticide concentration in runoff does not necessarily coincide with seasonal pesticide application patterns, especially in California, where rainfall events occur more frequently in the winter months (Budd et al., 2020; Wang et al., 2017). In urban landscapes, the "first flush" rain events of the water season can transport pesticides that have accumulated

during the dry season. Long term monitoring in agricultural and urban surface waters at CDPR monitoring sites have detected pesticides more frequently and at higher concentrations during storm events (Burant, 2021; Ensminger, 2021; Main, 2020; Wagner, 2020).

Several factors including storm characteristics, climate, watershed land use, and physicochemical properties of a pesticide can influence the transport of pollutants within a watershed. Storm characteristics, including the duration, intensity, timing, and amount of rainfall following pesticide application, can impact off-site transport of pesticides. California is among the most geographically diverse states; its climate conditions vary widely, with distinct regional weather patterns. Another site-specific factor influencing pesticide dynamics in the runoff is watershed characteristics including size, slope, topography, soil characteristics, and waterway substrate. Effects of the storm at sub-watersheds with varying characteristics directly influence the hydrograph shape and consequently its surface runoff (Viessman & Lewis, 2003). Watershed land use will influence both water transport pathways and pesticide use patterns. Impervious surfaces in urban settings may alter the hydrological response of a watershed to rainfall storms, directly affecting runoff volume, baseflow, peak flow, and flood risk (Arnold Jr. & Gibbons, 1996; Rezaei et al., 2019). Lastly, the physicochemical properties of the pesticide will determine the dominant environmental interactions that will influence its transport. These properties include water solubility, acid/base and ionic properties, sorption properties, and persistence (Gassmann et al., 2015; Larson et al., 1997). Pesticides of interest, commonly detected in surface waters, represent a wide range of solubilities and hydrophobicity, leading to a distribution of chemicals primarily transported in the dissolved phase to hydrophobic chemicals that are typically sorbed to sediment and organic material during transport.

Previous studies have attempted to characterize concentrations of pollutants transported in storm runoff. Urban first flush studies have described the pollutant peak concentration occurring before the hydrograph peaks (Casadio et al., 2010; Peter et al., 2020). The initial 20-30% volume of runoff from a first flush storm event can represent 60–90% of the total pollutant mass transported during a storm (Bach et al., 2010; Bertrand-Krajewski et al., 1998; Deletic, 1998; Kayhanian et al., 2008; McCarthy, 2009; Perera et al., 2021; Saget et al., 1996). A few studies have compared pollutant concentration profiles across the storm hydrograph (i.e., pollutograph) to different sampling strategies. Xing et al. (2013)

reported a considerable underestimation of pesticide residues (20–30%) and maximum concentrations (1 to 3 orders of magnitude) in storm runoff when comparing grab samples to automated samplers. The benefits of automated samplers as a possible sampling strategy include the possibility of samples to be taken at a rate proportional to the runoff flow (Gallé et al., 2020; Pitton et al., 2016; Rabiet et al., 2010; Xing et al., 2013). Therefore, it is important that existing monitoring protocols successfully achieve their purpose of measuring accurate pesticide concentrations without being misled by inappropriate temporal resolution (Chow et al., 2020; Peter et al., 2020).

CDPR's current characterization of pesticide residues includes the collection of storm runoff via grab samples or with the use of autosamplers (Teledyne Isco, Inc., Lincoln, NE) programmed to collect samples on a specific time interval, which are combined into one composite sample (Deng, 2021). Understanding how storm and basin characteristics influence the storm runoff process will enable CDPR to develop an effective sampling strategy of storm water runoff that targets peak or average concentrations. This focused study will provide information necessary to understand (1) the benefits and limitations of current and proposed sampling protocols, and (2) how well chosen sampling methods measure off-site movement of pesticides used in agricultural and urban settings.

2. Project Objectives

The objectives of the study are to:

1. Compare three sampling techniques (grab sampling, autosampler composite sampling, and autosampler individual sampling) on the characterization of pesticide concentrations in storm runoff. For each of these sampling techniques, we will:

    a. Determine peak and average pesticide concentrations in storm runoff within watersheds of various sizes;

    b. Evaluate the effect of various watershed characteristics on the transport of pesticides via storm-generated runoff: watershed size (larger vs. smaller watershed), slope, contributing land use, waterbody type (engineered conveyance vs. main stem), and stream substrate (natural vs. concrete-lined);

    c. Assess the effects of pesticide physicochemical properties (solubility, hydrophobicity) on peak and average pesticide concentrations in storm runoff;

    d. Evaluate the effects on the variability of storm characteristics on peak and average pesticide concentrations including rainfall intensity, duration and total precipitation.

3. Work to be Performed

Site selection

Site selection will be based on a number of factors (see Table 1) considered in tandem to optimize data collection necessary to answer the study objectives. Previous monitoring data will be summarized to narrow the choice of potential study sites based on pesticide detection frequencies. Sites with higher detection frequencies of pesticides of ecological concern will be prioritized. Available watershed data will be summarized for each site, including size, slope, waterbody type, and waterway substrate. A combination of characteristics (landscape, waterbody type, site type, watershed size and substrate) will be chosen to ensure a variety of watershed conditions are represented. Monitoring locations with associated flow monitoring equipment will be prioritized to allow for

mass transport estimations. Site selection will ensure that focal land uses (agricultural, urban) and specific waterbody types (engineered conveyance, main stem) are represented (Table 1). Four agricultural monitoring sites and four urban sites (n = 8) are proposed that best meet these factors. A fifth extra agricultural site will be considered due to possible runoff flow insufficiency.

Three storm events will be targeted for monitoring at each of the selected locations. At least one event for each location will target a first flush event. Storms will be chosen based on their predicted ability to generate sufficient runoff. Generated runoff varies drastically between sites with different watershed characteristics, so the choice to monitor will be left to the discretion of the monitoring project lead. It is difficult to ensure certain storm characteristics are met; however, all available storm information will be recorded. Storm information will be obtained from the National Oceanic and Atmospheric Administration (NOAA) and regional California Irrigation Management Information System (CIMIS) stations. If possible, the site hydrograph will be downloaded from the site-specific associated gauging station. Storm sampling events will be staggered between sites to accommodate limitations on laboratory capacity.

Table 1. Proposed monitoring sites.

Site ID	Project	Landscape	Waterbody Name	Site Type	Watershed Size	Substrate	Gauging Station	Onsite Storage Container
BAL	320	Urban	Ballona Creek	Waterway	300,751,200	Concrete	Yes	Yes
SC3	320	Urban	Salt Creek	Storm Drain	461,108	Concrete	Yes	Yes
SLC_LA	329	Urban	San Lorenzo Creek	Waterway	117,523,800	Concrete	Yes	Yes
FOL002	329	Urban	Upper American River	Storm Drain	257,913	Concrete	No	Yes
IC_INC	310	Ag	Ingram Creek	Waterway	59,622,300	Natural	No	No
CD_CBD	310	Ag	Colusa Basin Drain	Waterway	3,585,780,900	Natural	No	No
Sal_SanJon	321	Ag	Tembladero Slough	Ag Ditch	276,269,400	Natural	Yes	No
Sal_Hartnell	321	Ag	Tembladero Slough	Ag Ditch	72,463,500	Natural	No	No
Sal_Davis	321	Ag	Salinas River	Waterway	10,587,182,401	Natural	Yes	No

Sample collection

A monitoring study (grab sampling, autosampler composite sampling, and autosampler individual sampling) with replicated trials will be executed to monitor pesticides representing a wide range of physical and chemical properties. Grab samples will consist of water samples collected during each storm event,

collected directly into 1-liter amber glass bottles by hand or using a pole and then sealed with Teflon-lined lids following the CDPR's standard operating procedure (Deng & Ensminger, 2021). Three 6700 full-size autosamplers (Teledyne Isco, Inc, Lincoln, NE) will be installed at each monitoring site: one to collect a composite sample runoff throughout a storm event (time-weighted), and two additional ones, upgraded to a sequential sampling protocol with 12 1-liter glass bottles with caps. Sampling sites at or near United States Geological Survey (USGS) gauge stations (USGS, 2021) will allow plotting sampling times against the hydrograph. The timing of grab sample collection will be at the discretion of the monitoring team. Storm event duration varies widely in California and can exceed 24 hours. In such a scenario, sampling may exceed the holding time of chemical analysis compromising the quality of the results. Therefore, autosamplers will be set to collect runoff for the first 24 hours of a storm event to tentatively represent the rising and falling tails.

Samples will be transported on wet ice and then refrigerated at 4°C until analyzed. Dissolved oxygen, pH, specific conductivity, TDS, salinity, and water temperature will be measured *in situ* during each sampling event with an In-Situ Aqua Troll 500 multiparameter sonde (In-Situ; Fort Collins, CO, USA).

Chemical analysis

Chemical analyses will be performed by the Center for Analytical Chemistry at the California Department of Food and Agriculture (CDFA). A total of 61 pesticides (Appendix I) will be analyzed in each water sample collected from all sampling sites. Appendix I also presents the pesticide's associated analytical method reporting limits and method detection limits included in two analytical screens: a pyrethroid (PY) screen and liquid chromatography (LC) multi-analyte screen. Quality control (QC) will be conducted as described by Peoples (2019). Approximately 10% of all samples collected will be included for QC. Laboratory Quality Assurance/Qquality Control (QA/QC) will follow CDPR guidelines and will consist of laboratory blanks, matrix spikes, matrix spike duplicates, surrogate spikes, and blind spikes (Peoples, 2019). Laboratory blanks and matrix spikes will be included in each extraction set.

Data analysis

All data generated by this project will be entered into a Microsoft Office Access database that holds field information, field measurements, and laboratory

analytical data. The data generated from this investigation will be used to perform multiple statistical comparisons. Descriptive summary statistics will be performed for individual site and event, including peak and average concentrations for each of the three sampling techniques. Detection frequencies will be generated for each watershed and storm characteristic grouping. Non-parametric procedures will be used to statistically compare pesticide concentrations between sampling techniques (Appendix II). Regression analysis will be performed to evaluate the relative importance of an environmental parameter and its effect on peak and average pesticide concentrations.

4. Deliverables

1. Analysis report detailing monitoring results that will include evaluation of objectives 1a-1d.

2. A Standard Operating Procedure with guidance on how to collect storm water runoff, which will be utilized and referenced by future CDPR ambient monitoring projects, as well as a peer-reviewed journal article.

5. Estimated Timetable

Field Sampling: March 2023 – March 2026
Chemical Analysis: March 2023 – June 2026
Technical Report: April 2027

6. Personnel

The study will be conducted by staff from the Environmental Monitoring Branch, Surface Water Protection Program, under the general direction of Dr. Anson Main, Environmental Program Manager I (Supervisor). Key personnel are listed below:

Project Leader: Pedro Lima, Ph.D.
Co-Project Leader: Xin Deng, Ph.D.
Reviewing Scientist: Robert Budd, Ph.D.
Statistician: Xuyang Zhang, Ph.D.
Monitoring Team: Joshua Alvarado;
Rio Lininger;
Kari McClanahan;
KayLynn Newhart;
Mason Zoerner.
Analytical Chemistry: Center for Analytical Chemistry, CDFA.

Questions concerning this monitoring project should be directed to Dr. Pedro Lima, Sr. Environmental Scientist (Specialist), at (916) 324-4186 or by email at pedro.lima@cdpr.ca.gov

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8. Appendices

Appendix I. Reporting Limits and Method Detection Limits for pesticides in whole water.

Pesticide	CDFA Screen	Method Detection Limit (µg/L)	Reporting Limit (µg/L)
Abamectin	LC	0.004	0.02
Atrazine	LC	0.004	0.02
Azoxystrobin	LC	0.004	0.02
Bensulide	LC	0.004	0.02
Bifenthrin	PY	0.00091	0.001
Boscalid	LC	0.004	0.02
Bromacil	LC	0.004	0.02
Carbaryl	LC	0.004	0.02
Chlorantraniliprole	LC	0.004	0.02
Chlorpyrifos	LC	0.004	0.02
Cyfluthrin	PY	0.00146	0.002
Cypermethrin	PY	0.00154	0.005
Cyprodinil	LC	0.004	0.02
Desulfinyl Fipronil	LC	0.004	0.01
Desulfinyl Fipronil Amide	LC	0.004	0.01
Diazinon	LC	0.004	0.02
Diflubenzuron	LC	0.004	0.02
Dimethoate	LC	0.004	0.02
Diuron	LC	0.004	0.02
Esfenvalerate	PY	0.00166	0.005
Ethoprop	LC	0.004	0.02
Etofenprox	LC	0.004	0.02
Fenamidone	LC	0.004	0.02
Fenhexamid	LC	0.005	0.02
Fenpropathrin	PY	0.00132	0.005
Fipronil	LC	0.004	0.01
Fipronil Amide	LC	0.004	0.01
Fipronil Sulfide	LC	0.004	0.01
Fipronil Sulfone	LC	0.004	0.01
Fludioxonil	LC	0.004	0.02
Hexazinone	LC	0.004	0.02
Indoxacarb	LC	0.004	0.02
Isoxaben	LC	0.004	0.02
Kresoxim-methyl	LC	0.004	0.02

Lambda Cyhalothrin	PY	0.00174	0.002
Malathion	LC	0.004	0.02
Mefenoxam	LC	0.004	0.02
Methidathion	LC	0.004	0.02
Methomyl	LC	0.004	0.02
Methoxyfenozide	LC	0.004	0.02
Metribuzin	LC	0.004	0.02
Norflurazon	LC	0.004	0.02
Oryzalin	LC	0.004	0.02
Oxadiazon	LC	0.004	0.02
Permethrin	PY	0.00105	0.002
Prometon	LC	0.004	0.02
Prometryn	LC	0.004	0.02
Propanil	LC	0.004	0.02
Propargite	LC	0.004	0.02
Propiconazole	LC	0.004	0.02
Pyraclostrobin	LC	0.004	0.02
Pyriproxyfen	LC	0.004	0.015
Quinoxyfen	LC	0.004	0.02
Simazine	LC	0.004	0.02
S-Metolachlor	LC	0.004	0.02
Tebuconazole	LC	0.004	0.02
Tebufenozide	LC	0.004	0.02
Tebuthiuron	LC	0.004	0.02
Thiabendazole	LC	0.004	0.02
Thiobencarb	LC	0.004	0.02
Trifloxystrobin	LC	0.004	0.02

LC = Liquid chromatograph multi-analyte screen; PY = pyrethroids.

Appendix II. Non-parametric procedures frequently used for comparing paired data, two samples and three or more samples.

Data	**Non-Parametric Procedure**
Paired data	*Wilcoxon signed-rank test* for uncensored data; *Sign test* (modified for ties) for censored data with one reporting limit; *Score tests* for censored data with multiple RLs (the PPW test and the Akritas test).
Two Samples	*Wilcoxon rank-sum (or Mann-Whitney) test* or *Kolmogorov-Smirnov test* for censored data with one reporting limit; *Score tests* for censored data with multiple reporting limits (the *Gehan test* and generalized *Wilcoxon test*).

Three or more samples in one-way layout	*Kruskal-Wallis test* (for unordered alternative) or *Jonckheere-Terpstra test* (for ordered alternative) for censored data with one reporting limits; *Generalized Wilcoxon score test* for censored data with multiple reporting limits; *Multiple comparison* to detect which group is different.
Three or more samples in two-way layout	*Friedman's test* (for unordered alternative) or *Page's test* (for ordered alternative) for censored data with one reporting limits; *Multiple comparison* to detect which group is different.