Department of Pesticide Regulation
Environmental Monitoring Branch
1001 I Street
Sacramento, CA 95812

Study 289: Method Development for the Continuous Low-Level Aquatic Monitoring (C.L.A.M.) Sampler for Monitoring Urban Surface Water (FY2013-2014)

Michael Ensminger
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I. INTRODUCTION

Surface water monitoring typically consists of taking grab samples, where the sample is collected at a specific time and location. Grab samples only give a snap shot in time at a single event, and do not capture the overall picture of environmental pollution. Grab samples also may not detect pollutants that are in the environment at trace concentrations, where they vary over time, or from episodic pollution events. Fully automated samplers that take composite samples can overcome some of these disadvantages, but they are large, expensive, obtrusive, and only provide intermittent sampling (US EPA 2000, Vrana et al. 2005). Passive samplers are an alternative to both of these methods. Passive samplers are relatively simple and inexpensive, lacking the need for complicated, expensive field equipment and power that automated sampling equipment requires. They can be deployed for minutes to weeks or months and accumulate organic molecules based on the affinity of the receiving phase of the sampling device. This, often along with the length of their deployment time, allows them to detect bioavailable pollutants at very low concentrations, detect pollutants during episodic events, and detect variable pollutant concentrations (Vrana et al. 2005, Zabiegala et al. 2010). However, there are some drawbacks to these samplers, such as tearing of the membranes, and trapping sensitivity to temperature, water flow rate, salinity, and pH. They also are hampered with fouling during deployment and require extensive calibration studies and mathematical computation to obtain quantitative information (Vrana et al. 2005, Harman et al. 2012).

More recently, a sampler has been developed that may overcome some of these shortcomings and still retain simplicity. The C.L.A.M. (continuous low-level aquatic monitoring; C I Agent 2013) is an *in situ* submersible extraction sampler that will remove pesticides, PAH's, TPH's, and other trace organic pollutants from water. Because water is continuously drawn into the C.L.A.M. during deployment via a pump, the extraction volume (up to 100 L) can be estimated. After deployment, an extraction disk is removed from the C.L.A.M. and analyzed for the monitored pollutants. Because of the large volume of water that flows through the extraction disk, low reporting limits are achieved (C I Agent 2013). Although no peer-reviewed journal articles appear to be available for the C.L.A.M., several agencies have observed increased numbers of pesticides detected over routine grab sampling (Washington State Department of Ecology 2010, City of Los Angeles Watershed Protection Division and Environmental Monitoring Division 2011, USGS personal communication).

In the Sacramento area of California, the C.L.A.M. would appear to be an opportune sampler for capturing early pesticide runoff during rainstorm events. The median rainstorm event in the Sacramento, CA area is 48 hours; over 75% of all storms are 72 hours or less (Figure 1). This storm duration is suited to the length of operation of the C.L.A.M. (C I Agent 2013). Using the C.L.A.M. would eliminate speculating when to optimally collect grab samples for analyzing pesticide runoff. Ninety percent of the pesticide runoff occurs in the first 30% of a rainstorm event (McWayne 2013) and is the interval we want to capture. However, with grab sampling, this is not always feasible to attain due to the imprecision of storm prediction, logistics in getting staff to the sampling sites, having multiple sampling sites, safety, etc. The California Department of Pesticide Regulation (CDPR) has been routinely monitoring storm runoff since 2008 and has developed proficiency in monitoring storm events. However, even with this experience, sampling generally occurs after this 30% storm runoff and optimal pesticide runoff may be missed (Figure 2). Deploying the C.L.A.M. as rainfall begins through the length of the storm would ensure that the maximum pesticide load would be captured.

The study is designed to investigate using the C.L.A.M. in CDPR's urban monitoring project during rainstorm events. Initially, the C.L.A.M. will be deployed during non-rainstorm events to become familiar with its use and analysis, and to compare it to grab and composite sampling. Ultimately, full use during rainstorm events will be investigated.

II. OBJECTIVES

For FY 2013–2014, the objectives of this study are:

1) Investigate the temporal and spatial variability of selected pesticides detected by the C.L.A.M.;
2) Determine if the QC of the chemical analysis (surrogates, matrix spikes) during the analysis of C.L.A.M. disks after field deployment is acceptable;
3) Investigate the repeatability (precision) of the C.L.A.M. using field duplicate C.L.A.M. samplers;
4) Compare pesticide detections attained by the C.L.A.M. to traditional sampling, as grab and composite sampling;
5) Assess the feasibility of using the C.L.A.M. with storm sampling.

III. PERSONNEL

The study will be conducted by staff from the CDPR's Environmental Monitoring Branch, Surface Water Protection Program, under the general direction of Kean S. Goh, Environmental Program Manager I (Supervisory). Key personnel are listed below:

- Project Leader: Michael Ensminger, Ph.D.
- Field Coordinator: April Van Scoy, Ph.D.
- Senior Scientist: Frank Spurlock, Ph.D.
- Laboratory Liaison: Gail Cho
- Analytical Chemistry: California Department of Fish and Wildlife

Please direct questions regarding this study to Michael Ensminger, Senior Environmental Scientist (Specialist), at (916) 324-4186 or mensminger@cdpr.ca.gov.

IV. STUDY PLAN

Studies described herein are pilot studies to determine the accuracy and precision of using the C.L.A.M. as a monitoring sampler. Timelines stated below are estimated and any studies not completed in FY13-14 will continue in FY14-15.

Monitoring sites. Sampling will occur in Folsom or Roseville, CA, which are current monitoring areas for Study 269 (Ensminger 2013). For using the C.L.A.M., the water in the conveyances must be at least 6.5 cm deep (depth of C.L.A.M.). Many urban sites lack this depth during non-rainstorm events, but sites PGC010 in Roseville and TRP1 in Folsom have adequate depth. Other current monitoring sites could be slightly modified to accommodate the C.L.A.M. (e.g. FOL002, PGC022, PGC040).

Study Series 1: Initial C.L.A.M. deployment. This series of studies would determine if the results of the C.L.A.M. are repeatable by 1) using duplicate samplers in the field (field duplicates), and 2) using appropriate lab QC to ensure reproducibility (see section V, Chemical Analysis). These studies would partially meet objectives 1, 2, and 3 (also in study series 2 and 3, below). We will deploy the C.L.A.M. at two sites, likely at TRP1 and PGC010 during non-rainstorm events. TRP1 has good flow and is deep enough to accommodate the C.L.A.M. Although monitoring is limited at this site (only pyrethroids, fipronil, and synthetic auxin herbicides have been monitored), bifenthrin, fipronil amide, 2,4-D, dicamba, triclopyr, and MCPA have been detected. TRP1 encompasses one of the largest monitoring areas in Study 269, so other pesticides are expected to be detected with the C.L.A.M. We will also likely deploy the C.L.A.M. at PGC010. PGC010 has been used in CDPR's monitoring studies since 2008 and there is a high detection frequency of many pesticides, as 2,4-D, bifenthrin, and fipronil. PGC010 also is deep enough to contain the C.L.A.M. during non-rainstorm events, with adequate flow.

The initial deployment will be temporally replicated at each site (or more, dependent on lab QC), and field duplicate samples will be used at each site (Table 1; Appendix I). To ensure accurate flow measurements, C.L.A.M. calibrations will occur at deployment, once during deployment, and at the end of deployment.

Study Series 2: Comparisons of C.L.A.M. sampler to grab and composite sampling). Once we have sufficient data to ensure reproducibility with the C.L.A.M. analysis and field work, we will next attempt to determine if the C.L.A.M. sampler, at minimum, will give us the results we would expect from more traditional grab or composite sampling. Because the C.L.A.M. is a continuous sampler, extracting larger volumes of water (up to 100L), we would actually expect the C.L.A.M. to exceed grab or composite sampling results.

After the first studies are completed and QC accepted, the answer to this inquiry will be addressed by comparing the C.L.A.M. to grab and composite sampling. At one of the current sampling sites in Roseville or Folsom (likely PGC010 or TRP1), we will initiate a study to compare these three sampling methods. We want to use sampling sites and chose analytical screens where detection frequencies are high so that we can determine efficacy of the C.L.A.M. For this study, sampling will occur during a non-rainstorm event and include:

- A minimum 14 day antecedent dry period;

- Deploying two C.L.A.M. samplers at one site for 24 hr;
- Collecting grab samples at time = 0 and 24 hr for pyrethroids, synthetic auxin herbicides, imidacloprid, and fipronil analysis. One field duplicate and one field blank sample will be collected. These analyte groups are have the highest detection frequency in Northern California urban monitoring;
- Collecting one composite sample with an autosampler. The autosampler will be set to collect approximately 400 ml of water every hour (collecting about 10 L of water; 1-L samples will be sent to the lab for analysis per analyte group, plus one field duplicate sample).

This study will be replicated temporally (at least once, depending on field and lab QC) (Table 1, Appendix II). Additional studies could include using a pre-filter on the C.L.A.M. which would allow comparisons of the C.L.A.M. analysis as whole water samples. These studies would meet objective 4.

Series Study 3: Rainstorm sampling. The third set of studies would determine if the C.L.A.M. can be safely and accurately used during rainstorm events. Additional concerns during rainstorm monitoring emerge, as preventing the C.L.A.M. from moving from the sampling site with increased water flow, the effect of excess sediment load on the pump (and effect on determining accurate flow rates), safety during storm deployment/use, mid storm calibration (recommended by manufacturer), etc. These concerns will be addressed during a rainstorm monitoring event.

Assuming there will be several rainstorm events during 2Q 2014, we will deploy the C.L.A.M. during a rainstorm and compare the results to Study 269 (collected during the same rainstorm at the same site). At one site, two C.L.A.M.s will be deployed during one rainstorm event, 24 hr prior to the predicted rainstorm, 24 hr during the rain event, and then 24 hr after the rain event. C.L.A.M. sampling will be continuous over the 72 hr period (additional 24 hr periods may be required for more lengthy storms). The C.L.A.M. will be calibrated three times during a 24 hr deployment to more accurately determine flow rates. Multiple disk collections (new disks every 24 hr) will determine if using the C.L.A.M. when it is raining (i.e. storm runoff) increases detections/concentrations over when it is not raining (i.e. no storm runoff, pre- and post-storm). These studies would meet objective 5.

Field measurements. Water physiochemical properties (dissolved oxygen, electrical conductivity, pH, turbidity, and temperature) will be measured *in situ* during all sampling events with a calibrated YSI 6920 V2 meter (YSI Incorporated, Yellow Springs, OH, USA) (Doo and Lee 2008). Flow rates will be estimated with a Global portable velocity flow probe (Goehring 2008).

Sample Transport. CDPR staff will transport samples following the procedures outlined in CDPR SOP QAQC004.01 (Jones, 1999). A chain-of-custody record will be completed and accompany each sample. C.L.A.M. HLB disks will be removed from the C.L.A.M., placed in a sealed bag, and transported on ice.

V. CHEMICAL ANALYSIS

The Department of Fish and Wildlife, Water Pollution Control Laboratory, (CDFW) will conduct pesticide analyses for the C.L.A.M. studies. Reporting limits of the pesticides extracted from the C.L.A.M. are dependent of the total water uptake. Prior to using the C.L.A.M., CDFW will pre-wash HLB disks (used in the C.L.A.M.) with methanol and rinse with DI water to remove any contaminants on the disks. Also, CDFW will preload the disks with one or two surrogates prior to sampling.

Field QA/QC for the C.L.A.M. will comprise of field duplicate samples by placing two C.L.A.M. samplers side by side during sampling. For grab and composite water samples, we will collect field blank and duplicate samples. For acceptable field QC, relative percent differences in the analysis of field duplicates will be $\leq$ 25%, with no detections in field blanks. Laboratory QA/QC will follow CDPR guidelines and will consist of laboratory blanks, surrogates, matrix spikes, and matrix spike duplicates (Segawa 1995). Acceptable recovery for lab QC is 50-150% of the spiked amount.

VI. DATA ANALYSIS

We will use various nonparametric (e.g. Mann-Whitley or Wilcoxon rank-sum test) and/or parametric (e.g. paired t-tests) statistical methods to analyze the data. Skewness of the data will determine analysis type. Results from the C.L.A.M. sampler will be compared to field duplicates, grab samples, and composite samples.

VII. TIMETABLE

Field Sampling:	January 2014 – June 2014
Chemical Analysis:	January 2014 – October 2014
Summary Report:	April 2015

VIII. LITERATURE CITED

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Table 1. Estimated C.L.A.M. sampling for FY 2013-2014 (analysis by the California Department of Fish and Wildlife).

Sampling Date (expected)	Probable Site	No. of C.L.A.M. samplers	No. of C.L.A.M. deployments*	Total No. of C.L.A.M disks[§]	No. of extrac-tions[§§]	No. of grab & composite water samples
Initial C.L.A.M. deployment (1Q 2014) (Study 1)	TRP1	2	2-3[§]	8-12	2	0
	PGC010	2	2-3	8-12	2	0
Comparison to grab and composite samples (2Q 2014) (Study 2)	TRP1 &/or PGC010	2	1-2	4-8	1	15
Initial storm sampling and compare to grab sampling (2Q 2014) (Study 3)	PGC010	2	3-4	12-16	2	0**

* Dependent on lab QC; more deployments may be required

[§] Two HLB disks will be used per C.L.A.M. to prevent break through

[§§]Two extractions are required for polar and non-polar pesticide analysis

**Study 269 will collect grab samples

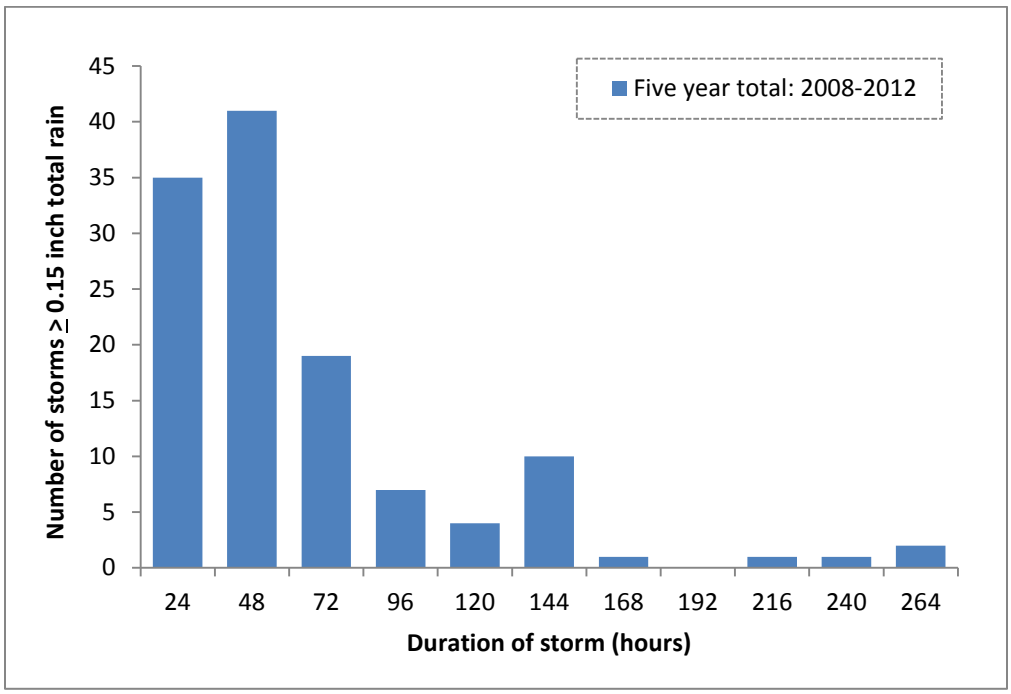

Figure 1. Number and duration of rainstorm events in the Sacramento, California area 2008 - 2012 (Fair Oaks, California station #131, http://www.cimis.water.ca.gov/cimis/)

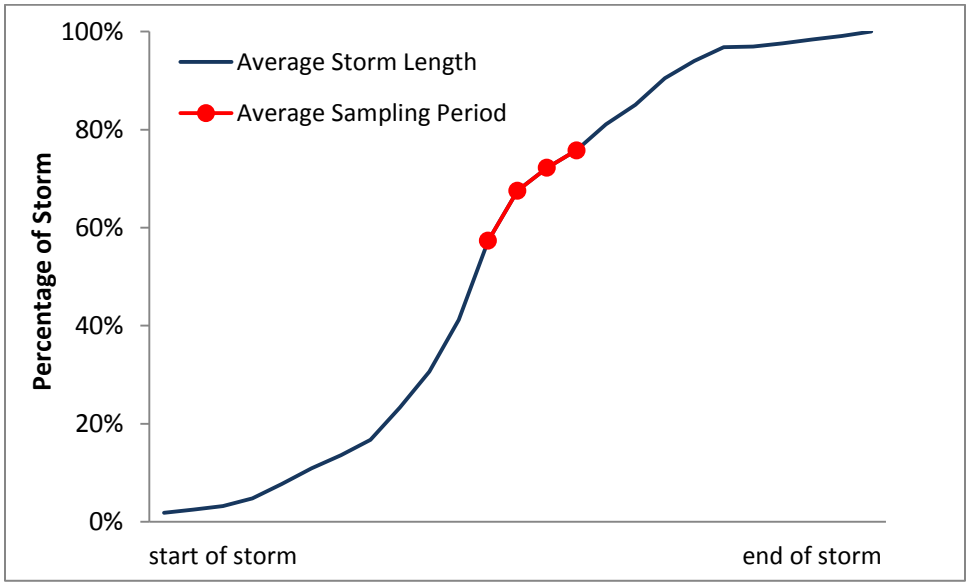

Figure 2. The California Department of Pesticide Regulation (CDRR) average storm sampling timings in the Sacramento area of Northern California (2008-2013). Line portion and graph markers in red are the average storm sampling period by CDPR staff (average of 12 storm events). Rainfall data is from the Fair Oaks, California station #131 (http://www.cimis.water.ca.gov/cimis/).

Appendix I. C.L.A.M. protocol treatment list for Study 1 (non-rainstorm sampling event)

Sample collection method	Site Id*	Analyte Group	QC**	Time of sample collection
C.L.A.M. unit 201	TRP1	Urban Screen[§]	none	24 hour continuous sample
C.L.A.M. unit 202 or 203			field duplicate	
C.L.A.M. unit 201	PGC010	Urban Screen	none	24 hour continuous sample
C.L.A.M. unit 202 or 203			field duplicate	

*Each site will be repeated temporally at least once; additional deployments may be needed if lab or field QC fails.

**Each C.L.A.M. HLB disk will be pre-rinsed to remove contaminants and treated with 1- 2 surrogates for lab QC. C.L.A.M. will be calibrated at time=0, 6-8, and 24 hr to ensure accurate flow calibrations.

[§]Urban screen: bifenthrin, carbaryl, chlorpyrifos, cyfluthrin, cypermethrin, deltamethrin/tralomethrin, diazinon, fenvalerate/esfenvalerate, fipronil + degradates, imidacloprid, lambda-cyhalothrin, malathion, permethrin, 2,4-D, diuron, imazapyr, MCPA, oryzalin, oxyfluorfen, pendimethalin, prodiamine, prometon, simazine, triclopyr

Appendix II. Comparison of C.L.A.M. sampler to grab and composite sampling (Study 2)

Sample collection method	Analyte Group*	QC**	Time (t) in relation to C.L.A.M. deployment
Grab	Pyrethroid	none	t=0 hr
Grab	Fipronil+degradates	none	t=0 hr
Grab	Imidacloprid	none	t=0 hr
Grab	Synthetic auxin herbicides	none	t=0 hr
Grab	Synthetic auxin herbicides	field blank	t=0 hr
Grab	Pyrethroid	none	t=24 hr
Grab	Fipronil+degradates	none	t=24 hr
Grab	Imidacloprid	none	t=24 hr
Grab	Synthetic auxin herbicides	none	t=24 hr
Grab	Synthetic auxin herbicides	field duplicate	t=24 hr
Composite	Pyrethroid	none	400 ml hourly/9.6 L 24 hr total volume; 1-L to lab per analyte group
Composite	Fipronil+degradates	none	
Composite	Imidacloprid	none	
Composite	Synthetic auxin herbicides	none	
Composite	Pyrethroid	field duplicate	
C.L.A.M. unit 201	Urban Screen[§]	none	24 hour continuous sample
C.L.A.M. unit 202 or 203		field duplicate	

*Based on location, other analyte groups may be substituted

**Each C.L.A.M. HLB disk will be pre-rinsed to remove contaminants and treated with 1- 2 surrogates for lab QC. The study will be repeated temporally at least once; additional deployments may be needed if lab or field QC initially fails. C.L.A.M. will be calibrated at time=0, 6-8, and 24 hr to ensure accurate flow calibrations.

[§]In this study, urban screen will be pesticides that can be analyzed with one (polar) extraction, likely: bifenthrin, carbaryl, chlorpyrifos, cyfluthrin, cypermethrin, deltamethrin/tralomethrin, diazinon, fenvalerate/esfenvalerate, fipronil + degradates, imidacloprid, lambda-cyhalothrin, malathion, permethrin, 2,4-D, diuron, imazapyr, MCPA, oryzalin, oxyfluorfen, prodiamine, prometon, simazine, triclopyr

Appendix III. Rainstorm event monitoring (Study 3). This study is at one site during a rainstorm event

Sample collection method	Analyte Group	QC*	Time of sample collection
C.L.A.M. unit 201	Urban Screen[§]	none	24 hour pre storm sample
C.L.A.M. unit 202 or 203	Urban Screen	field duplicate	
C.L.A.M. unit 201	Urban Screen	none	24 hour storm sample
C.L.A.M. unit 202 or 203	Urban Screen	field duplicate	
C.L.A.M. unit 201	Urban Screen	none	24 hour post storm sample
C.L.A.M. unit 202 or 203	Urban Screen	field duplicate	

*each C.L.A.M. HLB disk will be pre-rinsed and treated with 1- 2 surrogates for lab QC

[§]Urban screen: bifenthrin, carbaryl, chlorpyrifos, cyfluthrin, cypermethrin, deltamethrin/tralomethrin, diazinon, fenvalerate/esfenvalerate, fipronil + degradates, imidacloprid, lambda-cyhalothrin, malathion, permethrin, 2,4-D, diuron, imazapyr, MCPA, oryzalin, oxyfluorfen, pendimethalin, prodiamine, prometon, simazine, triclopyr

Note: C.L.A.M. will be calibrated at t=0, 6-12, and 24 hr to ensure accurate flow calibrations. Additional 24 hr periods may need to be added to study dependent on storm length