

Continuous low-level aquatic monitoring (CLAM) samplers for pesticide contaminant screening in urban runoff: Analytical approach and a field test case

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Highlights

- Surface water monitoring with the continuous low-level aquatic monitoring (CLAM) sampler.
- Developed a novel analytical method for extracting and analyzing organic pesticides from CLAM sampling disks.
- In field test cases, nine commonly used pesticides in urban environments were detected using the developed method.
- Detections using the CLAM sampler were more frequent and consistent than grab samples, but with lower concentrations.

Abstract

Monitoring of surface waters for organic contaminants is costly. Grab water sampling often results in non-detects for organic contaminants due to missing a pulse event or analytical instrumentation limitations with a small sample size. Continuous Low-Level Aquatic Monitoring (CLAM) samplers (C.I.Agent® Solutions) continually extract and concentrate organic contaminants in surface water onto a solid phase extraction disk. Utilizing CLAM samplers, we developed a broad spectrum analytical screen for monitoring organic contaminants in urban runoff. An intermediate polarity solid phase, hydrophobic/lipophilic balance (HLB), was chosen as the sorbent for the CLAM to target a broad range of compounds. Eighteen urban-use pesticides and pesticide degradates were targeted for analysis by LC/MS/MS, with recoveries between 59 and 135% in laboratory studies. In field studies, CLAM samplers were deployed at discrete time points from February 2015 to March 2016. Half of the targeted chemicals were detected with reporting limits up to 90 times lower than routine 1-L grab samples with good precision between field replicates. In a final

deployment, CLAM samplers were compared to 1-L water samples. In this side-by-side comparison, imidacloprid, fipronil, and three fipronil degradates were detected by the CLAM sampler but only imidacloprid and fipronil sulfone were detected in the water samples. However, concentrations of fipronil sulfone and imidacloprid were significantly lower with the CLAM and a transient spike of diuron was not detected. Although the CLAM sampler has limitations, it can be a powerful tool for development of more focused and informed monitoring efforts based on pre-identified targets in the field.

Keywords

- Active sampler;
- Grab sample;
- Pesticide;
- Solid phase extraction;
- Urban runoff

Abbreviations

- CDFW, California Department of Fish and Wildlife;
 - CDFA, California Department of Food and Agriculture;
 - CDPR, California Department of Pesticide Regulation;
 - CLAM, continuous low-level aquatic monitoring;
 - ESI, positive electrospray ionization;
 - HLB, hydrophobic/lipophilic balanced;
 - MDL, method detection limit;
 - RL, reporting limit;
 - RPD, relative percent difference;
 - SPE, solid phase extraction
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1. Introduction

Aquatic monitoring programs for organic chemical contaminants, especially pesticides, are often used to determine which contaminants are of concern to beneficial uses of surface waters. Pesticide monitoring is often conducted using a grab sampling approach, collecting samples at discrete time points, which can miss a pulse event. Grab sample volumes can also contribute to the limitations of analytical instrumentation to detect target analytes. Other approaches can be used in monitoring programs. Fully automated mechanical samplers that collect composite samples can overcome some of these disadvantages, but they are large, expensive, obtrusive, and only provide intermittent sampling ([Sisneroz et al., 2012](#) ; [Vrana et al., 2005](#)). Passive samplers are an alternative to both 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 ([Van Metre et al., 2017](#); [Vrana et al., 2005](#) ; [Zabiegala et al., 2010](#)). However, there are some drawbacks to these samplers, such as tearing of the membranes or trapping sensitivity to temperature, water flow rate, salinity, and pH. They also are hampered with biofouling during deployment and require calibration studies and mathematical computation to obtain quantitative information ([Harman et al., 2012](#) ; [Vrana et al., 2005](#)).

The Continuous Low-Level Aquatic Monitoring (CLAM) (C.I. Agent® Solutions) sampling method provides an alternative to these methods. CLAM samplers allow for low flow, active, and continuous aqueous extraction and concentration of organic contaminants in surface water flows and storm water runoff in the field. The samplers are small (length, 23.8 cm; diameter, 6 cm), lightweight (625 g), oblong-shaped submersible units, consisting of a solid phase extraction (SPE) disk, a pump, and a battery compartment. Water is continuously pulled through a small orifice (5 mm diameter) to the SPE disk for a measured time (24–48 h) and flow rate, resulting in a time integrated sample. The sample volume extracted can increase by two orders of magnitude compared to traditional water samples, providing significantly lower detection limits of target compounds in the environment. Only one peer reviewed article on the CLAM has been published, where increased numbers of chemical contaminants were detected over routine grab (discrete) sampling due to increased water sampled and lowered reporting limits (RLs) ([Coes et al., 2014](#)). In combination with land use activity information and spatial and temporal variability information of pesticide applications, CLAM samplers offer a powerful approach in determining pesticides of greatest concern in a watershed.

The Surface Water Protection Program in the Environmental Monitoring Branch of the California Department of Pesticide Regulation (CDPR) has been interested in alternative sampling methods for several years ([Adams, 2009](#)). More recently, the CLAM sampler has been introduced ([Kolok, 2012](#)) and the potential for obtaining time integrated samples was realized. In conjunction with the Water Pollution Control Lab, California Department of Fish and Wildlife (CDFW), CDPR has investigated the use of the CLAM sampler to replace or compliment traditional grab sampling. The goal of this study was to develop and validate an analytical methodology for a select suite of urban use pesticides and then apply this methodology to investigate herbicide and insecticide detections in urban runoff. Monitored pesticides were chosen based on CDPR's ongoing urban monitoring program ([Ensminger et al., 2013](#)). An intermediate polarity solid phase, hydrophobic/lipophilic balanced (HLB), was used as the sorbent for the CLAM disk to target a broad range of compound polarities in the environment.

2. Materials and methods

2.1. Study area and sampling

CLAM samplers were deployed at a storm drain outfall in Folsom, California (“TRP1”; latitude 38.64979, longitude -121.18014) five times in a 12-month period in 2015–2016. Water depth at the storm drain outfall was consistently 45 cm deep, with continuous flow (approximately 4.8 L s^{-1}), low sediment load (approximately 2.3 mg L^{-1}), and eventually emptied into the American River. CLAM samplers were deployed during non-rain events at TRP1. Duplicate CLAM samplers were assembled on site, installed with a single HLB disk, submerged, flow rate determined, and deployed up to 24 h. To maintain consistency with current CDPR analytical methods, pre-filters were not used in front of HLB disks to remove sediments. To reduce analytical costs only single HLB disks were used in this initial research. CLAM flow rates were determined at deployment, after approximately 6 h of deployment, and at termination by measuring the water volume output into a graduated cylinder. Average flow rates were calculated to determine the sample volume pumped, allowing for a concentration of organic contaminant to be calculated from mass analyzed from a SPE disk. When sampling ended, CLAM samplers were removed from the storm drain and HLB disks were placed individually into sealed bags; disks were transported on wet ice ($4 \text{ }^{\circ}\text{C}$) to CDFW within a few hours. HLB disks were refrigerated until extraction. All HLB disks were extracted within 28 days after sampling (except the initial deployment).

During the last deployment at TRP1, the CLAM samplers were compared to grab water samples (CDPR's typical monitoring method) and composite samples collected by Teledyne ISCO 6700 autosamplers (Teledyne ISCO, Inc). Two autosamplers were set up and collected time-weighted samples (15-min intervals) during the CLAM deployments. Both autosamplers collected 18.8 L of water in 23.5 h; two composited samples from each autosampler were sent to CDFW for analysis. Grab samples were collected in 1-L amber bottles at the initiation of CLAM deployment (“Day1 a.m.”), at the 6-h interval (“Day1 p.m.”), and at termination of the CLAM deployment (“Day2 a.m.”). In a final study, a sixth deployment was conducted in Orange County, California, at a storm drain outfall feeding into Salt Creek in Orange County (“SC3”; latitude 33.511933, longitude -117.697066). CLAM samplers were deployed during a rain storm event to determine the effect of storm runoff on CLAM uptake and subsequent laboratory analysis. The closest California Irrigation Management Information System (CIMIS) site, in San Clemente, California, recorded 2.4 cm of rain on March 6 and 7, 2016 ([CIMIS, 2016](#)). During this rain event the CLAM samplers were deployed for about 6 h.

Field duplicate samples and travel blanks were collected during each of the six deployments. With the water samples taken in the study comparison to CLAM samplers, a field blank sample was also collected. Water sample collections and the sample's chain of custody were conducted in accordance with CDPR's field methods ([Ensminger et al., 2013](#)).

2.2. Chemical extraction and analysis – CLAM disks

2.2.1. Pre-deployment conditioning

Prior to deployment, each HLB CLAM disk (Aqualytical HLB heavy capacity SPE disk, C.I. Agent Storm Water Solutions, P/N A50-HLB-CLAM disk) was conditioned by attaching a 50 mL syringe to the disk and pushing various solvents through the disk. Each disk rinsed with 50 mL ethyl acetate, 50 mL methanol, a 50 mL syringe volume of air, and 50 mL of DI water. After conditioning, two surrogates were spiked onto each disk at the laboratory, simazine-d₁₀ (2 mL of 0.2 or 100 µg L⁻¹) and fipronil-¹³C₄¹⁵N₂ (2 mL of 0.8 µg L⁻¹), followed by a final rinse of 50 mL DI water. These compounds were used as surrogates for analyte loss quantification during field deployment.

2.2.2. Extraction

Before extraction in the laboratory refrigerated CLAM disks were allowed to come to room temperature then attached to a vacuum manifold and dried for 1 h to remove residual water. Once dried, a surrogate compound (2 mL of 1.6 µg L⁻¹¹³C-atrazine) was spiked onto the disk to monitor extraction efficiency. The disk was then eluted with two 50 mL aliquots of 50:50 (v:v) methanol: acetonitrile using a 50 mL syringe. The eluate was rotary evaporated at 38 °C to approximately 3–5 mL and then brought to a final volume of 10 mL with methanol. The extract was filtered and an internal standard (diclofenac-d₄) was added before analysis by LC/MS/MS.

2.2.3. Analysis

The analysis of the target compounds was performed using an Agilent 1200 HPLC coupled to an Agilent 6410 triple quadrupole mass spectrometer. A Phenomenex Kinetex XB-C18 analytical column (2.1 mm × 100 mm × 2.6 µm) was used at a flow rate of 0.3 mL min⁻¹, a column temperature of 30 °C, and a 5 µL injection volume. For positive electrospray ionization (ESI) mode, the solvent gradient was as follows: 0–1 min, 90:10 water (0.1% formic acid): methanol (0.1% formic acid); 1–4 min, 40:60 water (0.1% formic acid): methanol (0.1% formic acid); 4–7 min, 20:80 water (0.1% formic acid): methanol (0.1% formic acid); 7–15 min, 20:80 water (0.1% formic acid): methanol (0.1% formic acid); 15–16 min, 90:10 water (0.1% formic acid): methanol (0.1% formic acid). For compounds analyzed using negative electrospray ionization mode, the solvent gradient was as follows: 0–2 min, 55:45 water (0.1% formic acid): methanol (0.1% formic acid); 2–8 min, 20:80 water (0.1% formic acid): methanol (0.1% formic acid); 8–14 min, 20:80 water (0.1% formic acid): methanol (0.1% formic acid); 14–15 min, 55:45 water (0.1% formic acid): methanol (0.1% formic acid). The ESI source parameters consisted of a drying gas flow of 11 L min⁻¹ at 350 °C, a nebulizer gas pressure of 40 psi, and a capillary voltage of 4000 V. Multiple reaction monitoring was used for the target analytes in both positive and negative ionization modes. The mass transitions and fragmentation parameters are presented in [Supplemental Information Table 1](#).

2.2.4. Validation studies

Method detection limits (MDL) were determined by spiking eight 1-L water samples with the target analyte list. The resulting standard deviation for each compound was multiplied by the student t factor corresponding to seven degrees of freedom. The reporting limit (RL) was calculated as four times the MDL ([Table 1](#)).

Table 1. Reporting limit ($\mu\text{g L}^{-1}$) calculations of pesticides from validation studies, based on 1-L water samples (FS = field surrogate).

Analyte	Mean ^a	Standard Deviation	MDL	RL
Carbaryl	0.018	0.0047	0.014	0.056
Chlorpyrifos	0.038	0.0062	0.019	0.074
Diazinon	0.004	0.0009	0.003	0.011
Diuron	0.229	0.0517	0.155	0.62
Fipronil (F)	0.019	0.003	0.008	0.033
F amide	0.103	0.0214	0.064	0.257
F desulfinyl	0.022	0.004	0.012	0.047
F desulfinyl amide	0.085	0.085	0.085	0.085
F sulfide	0.022	0.0034	0.01	0.04
F sulfone	0.021	0.0041	0.012	0.049
Hexazinone	0.019	0.0046	0.014	0.055
Imidacloprid	0.093	0.0208	0.062	0.25
Oryzalin	49.5	17.4	52.2	209
Oxyfluorfen	0.218	0.04	0.12	0.48
Pendimethalin	0.096	0.0216	0.065	0.259
Prodiamine	1.993	0.364	1.09	4.37
Prometon	0.019	0.0048	0.014	0.058
Simazine	0.045	0.0196	0.059	0.235
Simazine- <i>d</i> ₁₀ (FS)	0.192	0.048	0.142	0.57

a Mean of 8 replications. MDL = $2.998 \times \text{StdDev}$ ($\mu\text{g L}^{-1}$). Student t value for $df = 7$ is 2.998. RL = $4 \times \text{MDL}$.

A recovery study was conducted to evaluate the accuracy and precision of the analytical method over a broad concentration range. Three replicate 1-L water samples were spiked with all target analytes at 2, 5, 10, 20, and 100 times the reporting limit of each analyte. The water samples were loaded onto the CLAM disk and subsequently extracted and analyzed using the analytical approach developed for this study. Upper and lower control and warning limits were calculated based on the recovery study ([Supplemental Information Table 2](#)). A stability study was conducted to determine the length of time the CLAM disks could be held in the laboratory at 4 °C before analyte recoveries dropped below a threshold of 70%. Twelve CLAM disks were spiked at ten times the reporting limit and replicates of three were subsequently extracted and analyzed at $t = 0, 7, 28,$ and 60 days post spiking ([Supplemental Information Table 3](#)).

2.3. Chemical extraction and analysis – water samples

Grab and composite water samples were filtered using Whatman #5 filter paper (P/N 1005–090) to remove particulate prior to extraction. Two surrogate compounds, simazine-d₁₀ (0.2 mL of 100 µg L⁻¹) and fipronil-¹³C₄¹⁵N₂ (0.2 mL of 400 µg L⁻¹) were spiked into a 500 mL pre-filtered water sample prior to loading onto a pre-conditioned Oasis® HLB SPE cartridge (6 cc x 200 mg, Waters Corporation, P/N WAT106202) under vacuum. The cartridge was then dried under vacuum for 5 min prior to elution with 2 mL of 50:50 (v:v) methanol: acetonitrile. The extract was filtered and an internal standard (diclofenac-d₄) was added before analysis by LC/MS/MS.

3. Results and discussion

3.1. Laboratory quality control data

¹³C-Atrazine, simazine-d₁₀, and fipronil-¹³C₄¹⁵N₂ were used as surrogates to determine extraction efficiency and field quantification loss ([Supplemental Information Table 4](#)). Recoveries of ¹³C-atrazine and fipronil-¹³C₄¹⁵N₂ suggest that matrix effects decreased recoveries, and therefore field results in general may have been reduced. ¹³C-Atrazine recoveries ranged from 16 to 141%. Travel blanks had the highest recovery (65–141%) with field disks having the lowest (16–58%). Fipronil-¹³C₄¹⁵N₂ recoveries ranged from 10 to 77%. Again, travel blanks had the highest recovery (73–77%) whereas field disks had poor recoveries (10–38%). Simazine-d₁₀ recoveries were poor in all disks spiked with 0.2 µg L⁻¹ simazine (0–55% recovery) but were acceptable in disks spiked with 100 µg L⁻¹ (73–104% recovery), suggesting laboratory difficulties extracting simazine lower concentrations, field matrix effects, or both.

3.2. Pesticide detections and field quality control

3.2.1. Reporting limits

RLs were generally lower with the CLAM than the 1-L water samples, due to higher volumes of water pumped through the CLAM. On the March 1, 2016, deployment when water samples were compared to the CLAM, CLAM RL's were 1.6–200 times lower; nine pesticides had RL's generally less than 1 ng L⁻¹ ([Fig. 1](#)). If pumping volumes remained high, CLAM RLs were lower than those of water analysis ([Fig. 2](#)). However, some CLAM RLs were higher than their respective RLs obtained through traditional 1-L water analysis until the volume pumped through the CLAM exceeded 17–23 L. Thus, the CLAM needs to be used in situations where at least this amount of water can be pumped. The RL of oryzalin was quite high in both CLAM and water, as were the water RLs for oxyfluorfen and prodiamine ([Fig. 1](#) ; [Fig. 2](#); [Supplemental Information Tables 5 and 6](#)).

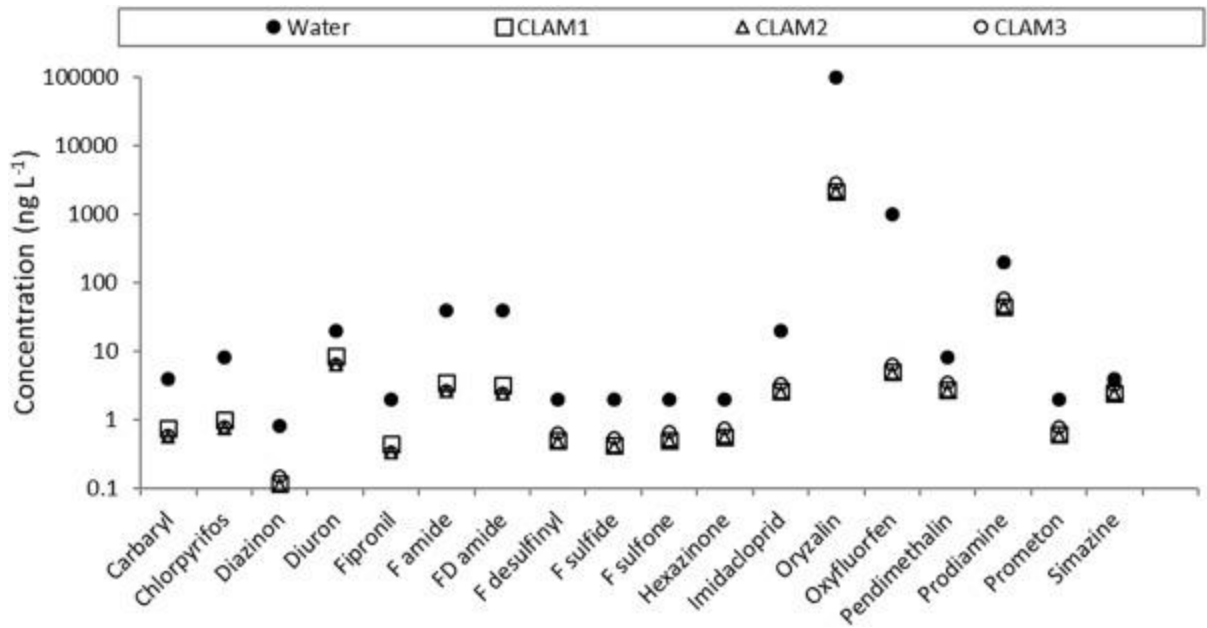


Fig. 1. CDFW reporting limits (RL) of the CLAM compared to water samples from the March 1, 2016 deployment (F = fipronil; FD = fipronil desulfanyl). CLAM1, CLAM2, CLAM3 are the three separate CLAM samplers that were deployed at the sampling site TRP1.

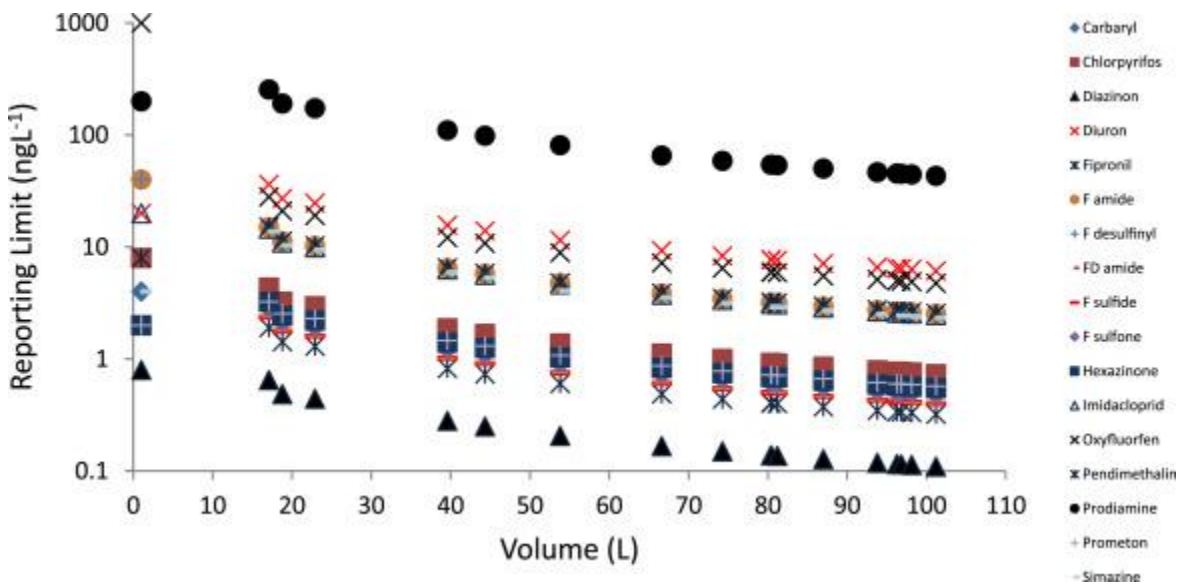


Fig. 2. Reporting limit changes with volume of water pumped through the CLAM (1-L of water is CDFW's reporting limit for water samples; all other volumes are from the CLAM). Oryzalin was omitted due to its high reporting limit (CLAM, 2064–12,216 ng L⁻¹; water, 100,000 ng L⁻¹), but follows the same trend.

3.2.2. Detections

During the six different deployment dates, with 15 CLAM deployments (including field duplicates), nine pesticides or pesticide degradates were detected. Imidacloprid, fipronil, and several fipronil degradates (amide, sulfide, sulfone) were the most frequent detections ([Fig. 3](#); [Supplemental Information Table 5](#)). Prometon was detected in three sampling events, and fipronil desulfanyl, diuron, and hexazinone were detected in one sampling event. Nine pesticides were never detected with the CLAM (carbaryl, chlorpyrifos, diazinon, fipronil desulfanyl amide, oryzalin, oxyfluorfen, pendimethalin, prodiamine, and simazine). For all but prodiamine and oxyfluorfen, RLs were low (0.1–28 ng L⁻¹) suggesting that there were no or very low levels of these pesticides in the sampled water. In some cases, RLs for prodiamine were greater than concentrations known to occur in urban runoff which would limit detections ([Ensminger et al., 2013](#)). However, for oryzalin, CLAM RLs were quite high (2064–12,216 ng L⁻¹) likely limiting detections if it was present in the runoff water. Travel blanks were used with each sampling date. None of the travel blanks had detections of any of the targeted pesticides ([Supplemental Information Table 4](#)). One field blank grab sample taken during the CLAM comparisons to water samples had no detections of any of the pesticides.

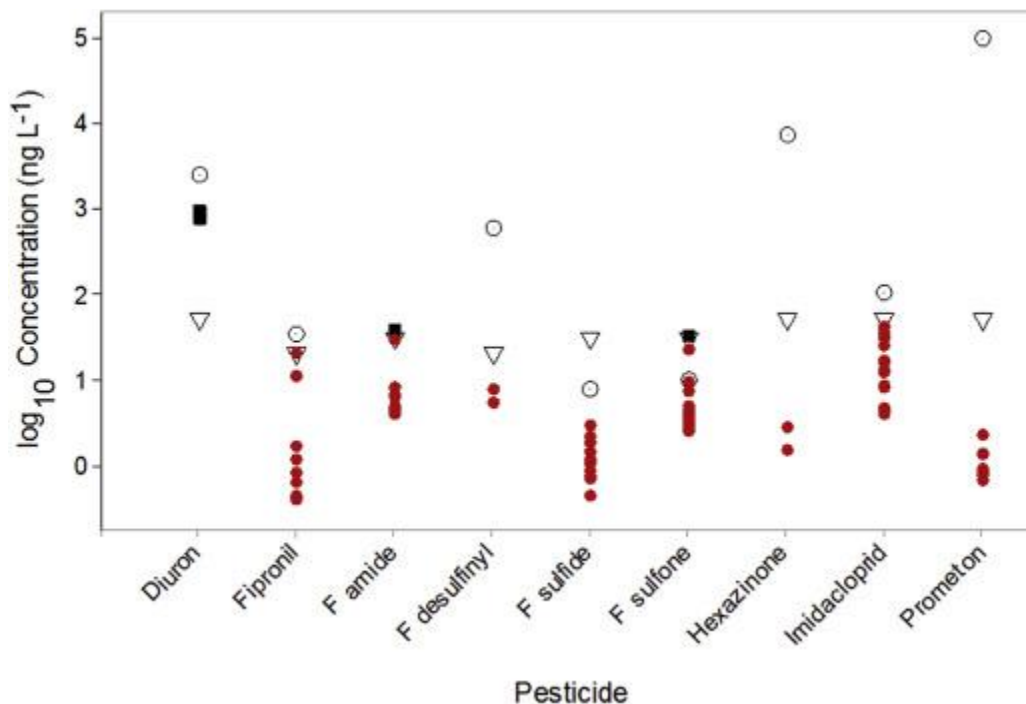


Fig. 3. Pesticide detections using the CLAM samplers. Red circles denote detections below CDFA's reporting limits. Black squares denote detections at concentrations above CDFA's reporting limits (open triangles, CDFA RL). Open circles are aquatic toxicity thresholds (for imidacloprid, see [Anderson et al., 2015](#); for fiproles, see [Weston and Lydy, 2014](#); for herbicides, US EPA aquatic benchmarks [<https://www.epa.gov/pesticide-science-and-assessing-pesticide-risks/aquatic-life-benchmarks-pesticide-registration>]; no toxicity data for fipronil amide available). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

These results show the power of the CLAM for use as a monitoring tool. The California Department of Food and Agriculture (CDFA) conduct CDPR's routine, ambient monitoring pesticide analysis ([Ensminger et al., 2013](#) ; [Budd et al., 2015](#)). Comparing CDFA's RLs to the detections with the CLAM, all detections, except four, were at concentrations below CDFA's RLs ([Fig. 3](#)). This provides valuable monitoring information, especially at the TRP1 monitoring site where most of this field work was conducted. CDFA analysis of water grab samples from CDPR's ambient monitoring program would show that this urban drainage site has no detections of fipronil or imidacloprid, and therefore these pesticides are not a concern. However, the CLAM gives a different story; fiproles and imidacloprid are common contaminants of the runoff from this urban neighborhood. Detections with lower RLs, however, may not indicate an environmental concern. Of the detected pesticides in this study, only fipronil sulfone and fipronil sulfide have CDFA RLs that are higher than aquatic thresholds, where utilization of the CLAM would benefit characterizing their individual potential toxicity ([Fig. 3](#)). Lower RLs that can provide uncensored data may also be needed to make decisions for monitoring site selection and additional (traditional) monitoring, determining additive or synergistic effects, trend analysis, or for determining effectiveness of regulations or label changes.

3.2.3. Precision among CLAM field duplicates

In addition to determining if pesticides could be detected at concentrations below CDFA's RLs, a main focus of this study was to determine the precision of the field sampling and subsequent laboratory analysis when using the CLAM. Relative percent differences (RPDs) were used to determine acceptance; 25% differences or less were used as a level of acceptability (Gail Cho, Quality Assurance Officer, CDFW, personal communication). RPDs from the first deployment were unacceptable for all detected pesticides except for fipronil sulfone (RPD, 24%; [Fig. 4](#)). The HLB disks were not analyzed within the 28 day holding time and this may have accounted for the lack of precision (laboratory method development was still being investigated at this deployment). After further laboratory method development and with new field deployments, all other four dry season monitoring results generally gave acceptable RPDs for the detected pesticides ([Fig. 4](#)). Two RPDs were slightly higher than the 25% acceptable, but taken as a whole among field duplicate samples and sampling dates, differences among analyses were acceptable.

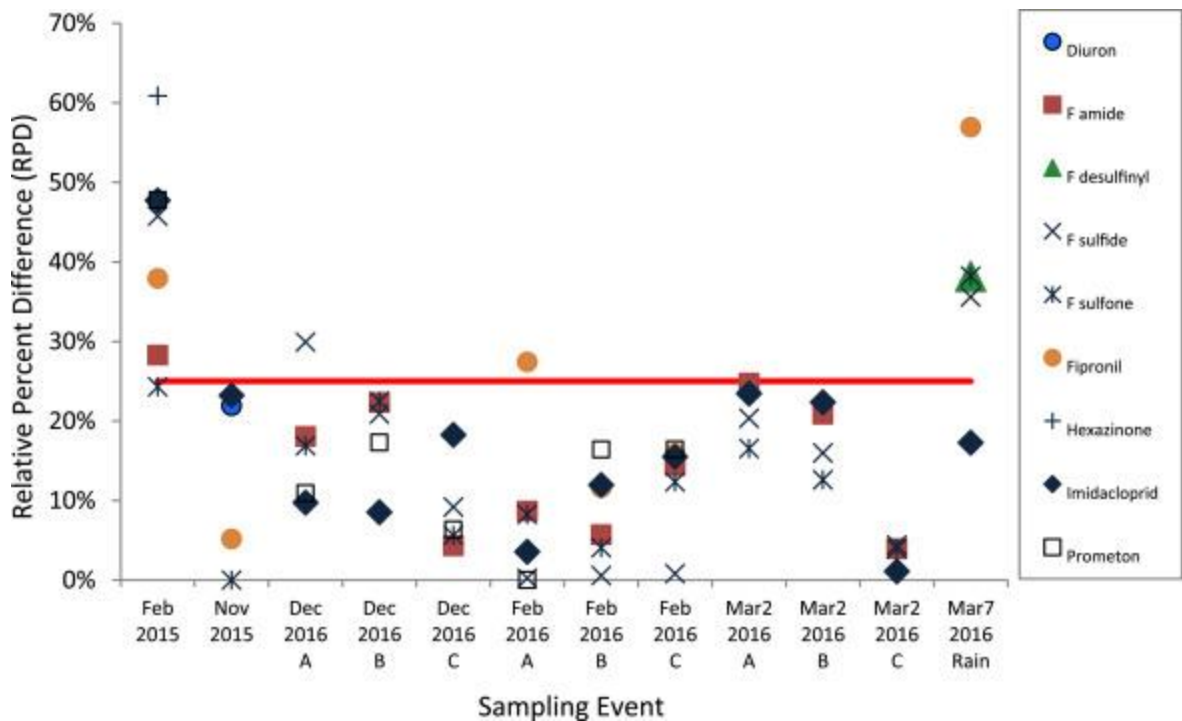


Fig. 4. Relative percent differences (RPD) for the pesticide analysis. In the November 2015 analysis, fipronil sulfone was detected in the field sample (4.1 ng L^{-1} , reporting limit = 1.6 ng L^{-1}) but the field duplicate sample was not detected and RPD could not be calculated. Sampling times with an “A”, “B”, or “C” are differences among field duplicate samples. Red line is the acceptable level of RPD (25%).

On March 7, 2016, the CLAM was deployed at a different site during a rain storm event. Fiproles (fipronil and degradates) and imidacloprid were detected. RPDs among the fiproles were unacceptable, ranging from 36 to 57%, whereas the imidacloprid RPD was acceptable (17%). The effect of storm runoff (higher flow or higher sediment loads) or shorter sampling time (6 h vs. about 24 h in dry weather sampling) may be interfering with extraction and analysis for fiproles. Fipronil is more hydrophobic than imidacloprid and thus are more likely to bind to sediments (Bonmatin et al., 2015). Increased sediment loads may be interfering with fiprole analysis; however, sediments were not measured during this or other sampling events. Using the CLAM for storm sampling warrants further investigation.

3.2.4. Detection accuracy

With the final deployment at Folsom site TRP1, three CLAM samplers were compared to grab water samples (three samples taken over 24 h) and time-weighted samples taken with autosamplers. CDPR typically takes grab samples in its surface water monitoring programs, and this is the measure we are using for accuracy or expected results. CLAM samples consistently detected more pesticides than the other sampling methods (Supplemental Information Table 7). Each of three CLAM samplers detected imidacloprid, and three fipronil

degradates (amide, sulfide, sulfone). Grab water samples and autosamplers detected both imidacloprid and fipronil sulfone, except one grab sample (“Day2 AM”) did not detect imidacloprid. The first day morning grab sample also detected fipronil sulfide, but other water samples did not detect this fipronil degradate. The first day grab water taken in the afternoon (“Day1 PM”) also detected diuron where the CLAM and autosamplers did not. In the water samples, diazinon, pendimethalin, and simazine were suspected of being detected but not confirmed. Diazinon was reported in the field duplicate of the autosampler composite sample, but not its corresponding water field sample. Reported detections were near the RL (two samples analyzed; 0.9 and 1 ng L⁻¹; RL, 0.8 ng L⁻¹). Pendimethalin was reported in the field sample of the “Day1 PM” grab sample, but not in its corresponding field duplicate (taken at the exact identical time with a two-pole sampler). The pendimethalin result was at its RL (8 ng L⁻¹). Simazine was reported in one sample of the original field autosampler composite sample, but not in a corresponding field sample or field duplicate sample taken at the identical time (detection, 4 ng L⁻¹; RL, 8 ng L⁻¹). The inconsistent results in the water samples make it difficult to determine the actual presence of these pesticides in the runoff water. They were not detected in the CLAM; it is uncertain if this is a weakness of the CLAM or an artifact of the water analysis.

Of the two chemicals detected by all three sampling methods (imidacloprid and fipronil sulfone), CLAM concentrations were significantly lower than water concentrations ([Fig. 5](#)). [Coes et al. \(2014\)](#) previously showed CLAM samples have lower concentrations than grab samples, although there were no direct comparisons with pesticides. In this study, with only two direct comparisons, additional work is warranted to determine pesticide detection accuracy with the CLAM. Lower concentrations from CLAM samples may be due to particle non-retention on the HLB disk. In this study, we did not specifically evaluate for breakthrough, and this may have also accounted for lower concentrations by the CLAM samplers. However, in an early deployment, battery failure interrupted one of the CLAM deployments. This CLAM deployment was halted after 6 h; new batteries and HLB disk were installed and the CLAM was run for an additional 17 h. Similar concentrations of diuron, fipronil, and imidacloprid were detected by this CLAM and its field duplicate sample (a second CLAM deployed), suggesting breakthrough is not an issue for these pesticides when the CLAM is used for up to 24 h. Reduced concentrations by the CLAM samplers may have been due to matrix effects, as suggested in the results from the surrogate field samples ([Supplemental Information Table 3](#)).

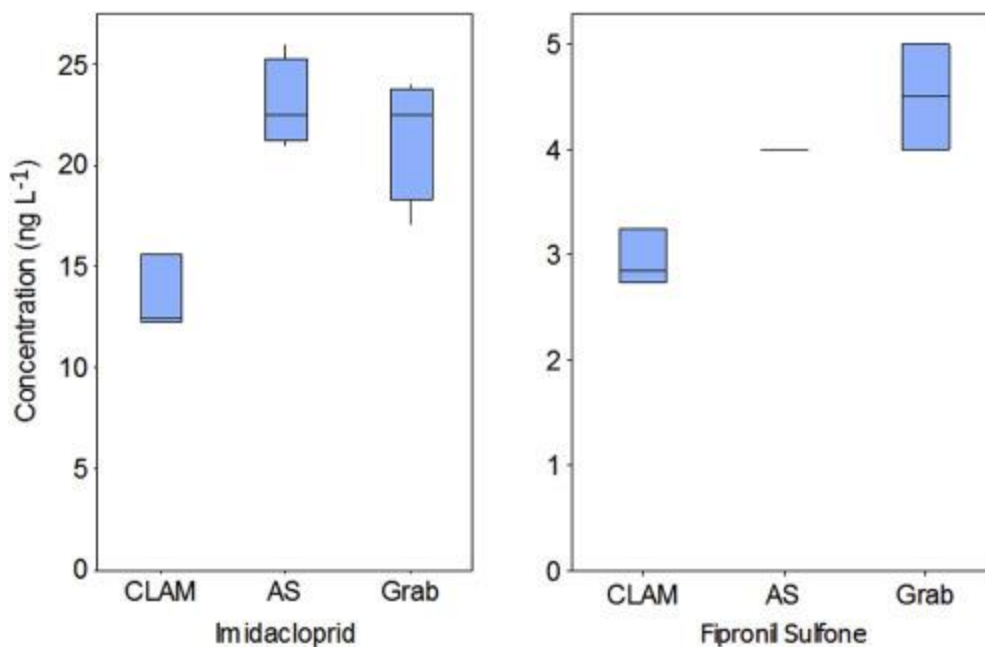


Fig. 5. Comparison of concentrations by the CLAM sampler (CLAM), autosampler (AS), and grab samples for the March 1, 2016, deployment at monitoring site TRP1. CLAM detections were significantly lower (Kruskal-Wallis nonparametric test) for imidacloprid ($p = 0.047$) and fipronil sulfone ($p = 0.018$).

A disadvantage of the CLAM may be that it does not give an optimal quantitative value for a pesticide, which could underestimate environmental concerns. However, the CLAM can give good evidence that a pesticide may be a frequent contaminant when 1-L water samples do not. In the side-by-side comparison, fipronil sulfide was detected in one grab water sample (“Day 1 AM” sample). Other grab samples and autosamplers reported trace detections of this chemical. Likely, there was little difference in concentrations among these samples. However, fipronil sulfide was detected in all three CLAM samplers, giving confidence that trace detections were true. In addition, the CLAM samplers also detected fipronil amide, which the water samples did not. Detections of all three degradates in the CLAM gives confidence that fipronil is in the runoff from this urban catchment area and the CLAM gives a higher signal for fipronil being a pesticide of concern than water samples (grab or autosamplers) do. Water samples alone make this a tenuous conclusion, but the CLAM consistently shows that fiproles are in this catchment area.

Another disadvantage of the CLAM is its failure to capture very brief spikes of pesticide in the water column. The CLAM may not be able to pump enough water in a brief time period to allow for a detection. This could be the case for the diuron detection in the grab sample (Day 1 p.m.) but not in the CLAM or autosamplers. This would not appear to be a serious disadvantage for the CLAM. As grab samples give only a snapshot of the water column for a very specific

time, monitoring programs likely will not consistently collect pesticide peaks. Overall, the data show that the CLAM gives more consistent detections than water samples.

4. Conclusions

Monitoring programs aim to determine areas and pesticides of concern. The method of monitoring can influence conclusions made by these monitoring programs. For example, in CDPR's urban monitoring programs, fipronil and imidacloprid have more detections in Southern California than in the northern areas of the state; this has been assumed to be due to higher pest pressures and use ([Budd et al., 2015](#) ; [Ensminger et al., 2013](#)). But lack of detections may be due to concentrations below reporting limits in these areas. Here, we describe a method to extract and analyze eighteen pesticides from HLB disks from field deployments of the CLAM dynamic sampler that allows for lower RLs. Pesticides selected were based on CDPR's monitoring program and cover a range of pesticide classes and solubility. During non-rain events, CLAM samplers were deployed at one site in Folsom, California to determine precision and accuracy of these samplers. During one final deployment, the CLAM samplers were deployed at a site in Orange County during a rainstorm event to observe the effect of storm runoff on sampling, extraction, and analysis.

This study concluded that the CLAM analysis gives lower RLs, more consistency, and more confidence than water samples (grab samples or time-weighted samples), especially with detections near traditional grab sampling RLs or with trace detections (between MDL and RL). In this study, we have discussed how fiproles and imidacloprid are pesticides of environmental interest because of their frequent detections by the CLAM, which has not previously been determined with traditional grab sampling by CDPR at this sampling site in Folsom, California. The analytical methods described here give good reproducibility when the CLAM is deployed during non-rain sampling events with low sediment loads. The CLAM had no issues with biofouling, disk tearing, or mechanical malfunctions. Measuring CLAM flow rates allowed for determination of quantitative data from total pesticide mass extracted from disks.

Additional research that was not investigated during this study is needed and currently provides uncertainties for the CLAM when used for pesticide research. These include investigating breakthrough, increasing the spectrum of pesticides, alternative disks (C-18), and determining the influence of environmental factors (e.g., temperature, pH, flow rates, and sediment load) on pesticide retention and analysis. Also, additional studies are needed comparing traditional grab samples to the CLAM as this study only compared two pesticides in one side-by side evaluation. Currently, the CLAM may not replace traditional grab sampling but can be used to investigate potential monitoring areas for more intensive monitoring via traditional sampling.

Disclaimer

The mention of commercial products, their source, or use in connection with material reported herein is not be construed as either an actual or implied endorsement of such products by the CDFW or CDPR.

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Appendix A. Supplementary data

The following is the supplementary data related to this article:



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