Continuous Low-Level Aquatic Monitoring and Alternative Time-Integrated Sampling Method

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Background:

California Department of Pesticide Regulation's (CDPR) Surface Water Protection Program (SWPP) relies on surface water monitoring to help protect the aquatic environment from the impacts of pesticides and their degradates. Monitoring typically involves the collection of 1-L water grab samples, which are then extracted and analyzed (Figure 1). SWPP has been interested in alternative sampling methods such as the continuous low-level aquatic monitoring (CLAM) sampler (Figure 2). The CLAM is a dynamic sampler that is light weight, easy to use, assembled onsite, and contains a disk that sorbs chemicals via active pumping of water. In collaboration with the California Department of Fish and Wildlife (CDFW), a method was developed to extract commonly detected pesticides in urban runoff from the CLAM (Vasquez et al., 2017).

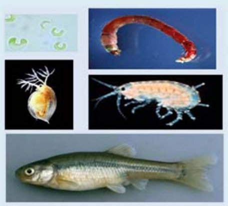

Figure 1. Aquatic species of concern in surface water

Objective:

- Determine feasibility of using the CLAM sampler for surface water monitoring (assess precision and accuracy).

Figure 2. The entire components for the CLAM

Methods:

- CLAM deployed at an urban site in Folsom, CA (Figures 3 and 4).
- CLAM deployment lasted for about 24 hours.
- CLAM deployed four different times from 2015–2016 during non-storm events, using field duplicates to measure precision.
- During final deployment, the accuracy of the CLAM sampler was measured by comparing CLAM results to composite water samples collected by autosamplers (ISCO® 6700 portable sampler) and 1-L grab samples.
- Analytical method by CDFW (Vasquez et al., 2017).

Figure 3. CLAM deployment in Folsom, CA

Figure 4. CLAM arrangement during deployment in Folsom, CA

Results:

- After deployment, CLAM disks contained sediment but generally had good linear decrease in flow during deployment indicating general decrease of battery life (Figure 5).
- Lower reporting limits (RL) were observed when using the CLAM sampler than with traditional 1-L grab sample RLs (CDPR, 2013) except for prodiamine (Figure 6).
- 7 different pesticides or pesticide degradates were detected during the CLAM deployments (Figure 7).
- Precision among CLAM samples were generally within laboratory-accepted range (≤25% RPD)(Figure 8).
- Pesticides were detected more consistently with the CLAM (Table 1) but exhibited lower concentrations than water samples (Figure 9).

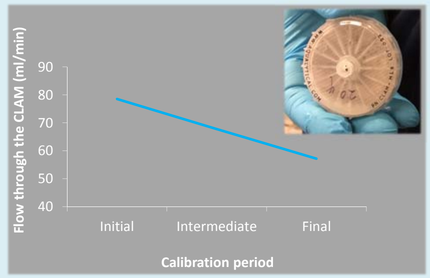

Figure 5. Average flow throughout deployment. Lower final flow due to battery life. Picture insert, image of CLAM disks after deployment included.

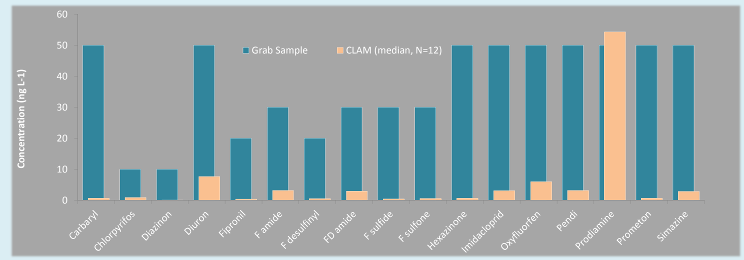

Figure 6. Comparison between grab samples and CLAM reporting limits (F = fipronil; D = desulfinyl; Pendi = pendimethalin)

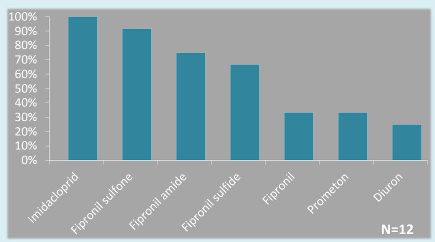

Figure 7. Detection frequency of pesticides from the CLAM sampler

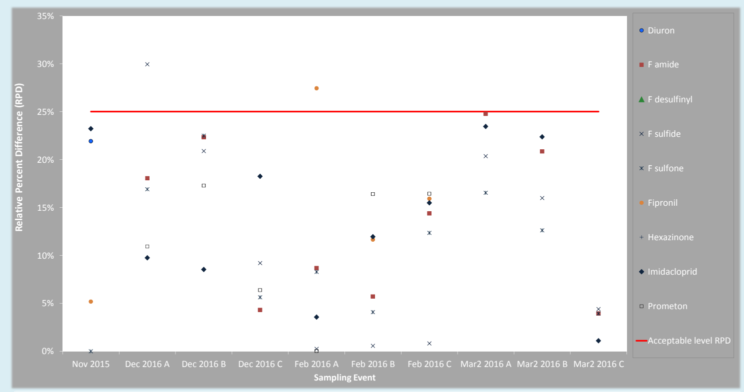

Figure 8. Relative percent differences of the pesticides detected using the CLAM sampler. A,B,C represent different repetitions during the same sampling date.

Table 1. Detections by CLAM, grab, and automated samplers in the last deployment (Norm = field sample; FD = field duplicate sample; sample = 1–3 different grab samples taken over 24 h)

Pesticide	CLAM			1-L Grab			Autosampler	
	Norm	FD1	FD2	1	2	3	Norm	FD
Fipronil amide	X	X	X					
Fipronil sulfide	X	X	X	X				
Fipronil sulfone	X	X	X	X	X	X	X	X
Imidacloprid	X	X	X	X	X		X	X

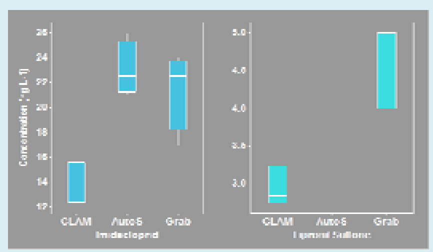

Figure 9. Concentration differences of imidacloprid and fipronil sulfone with different sampling methods. (AutoS = Autosampler)

Conclusion: CLAM is an alternative environmental assessment tool that can detect low concentrations of pesticides in surface water, which may subsequently warrant additional monitoring and evaluation. This approach has the ability to stretch limited sampling budgets while maximizing the ability to obtain relevant chemistry data.

References.
CDPR. 2013. Analytical methods. http://cdpr.ca.gov/docs/emon/pubs/em_methd_main.htm

Vasquez, M., S. Mohammed, H. Tsai, G. Cho, M. Ensminger. 2017. Continuous low level aquatic monitoring (CLAM) samplers for organic contaminant screening in urban runoff: Development of an analytical approach. 253rd American Society Meeting, San Francisco, CA. https://ep70.eventpilot.us/web/page.php?page=IntHtml&project=ACS17SPRING&id=2648592

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