

# The Potential of POCIS and SPMD Passive Samplers to Measure Pesticides in California Surface Waters

## Supplemental Material

### **Monitoring of Folsom's Constructed Wetland:**

In Folsom, the inlet and outlet of a constructed wetland (WLI and WLO) were monitored for pesticides to evaluate the pesticide removal efficiency through the wetland. The wetland was monitored simultaneously with the two main sites in spring and summer, using the simplified regime as that for the spring and fall deployments. Due to space restrictions, the wetland evaluation only included grab sampling and SPMDs, thus focusing on the more hydrophobic compounds including the pyrethroid insecticides (main report Table 1).

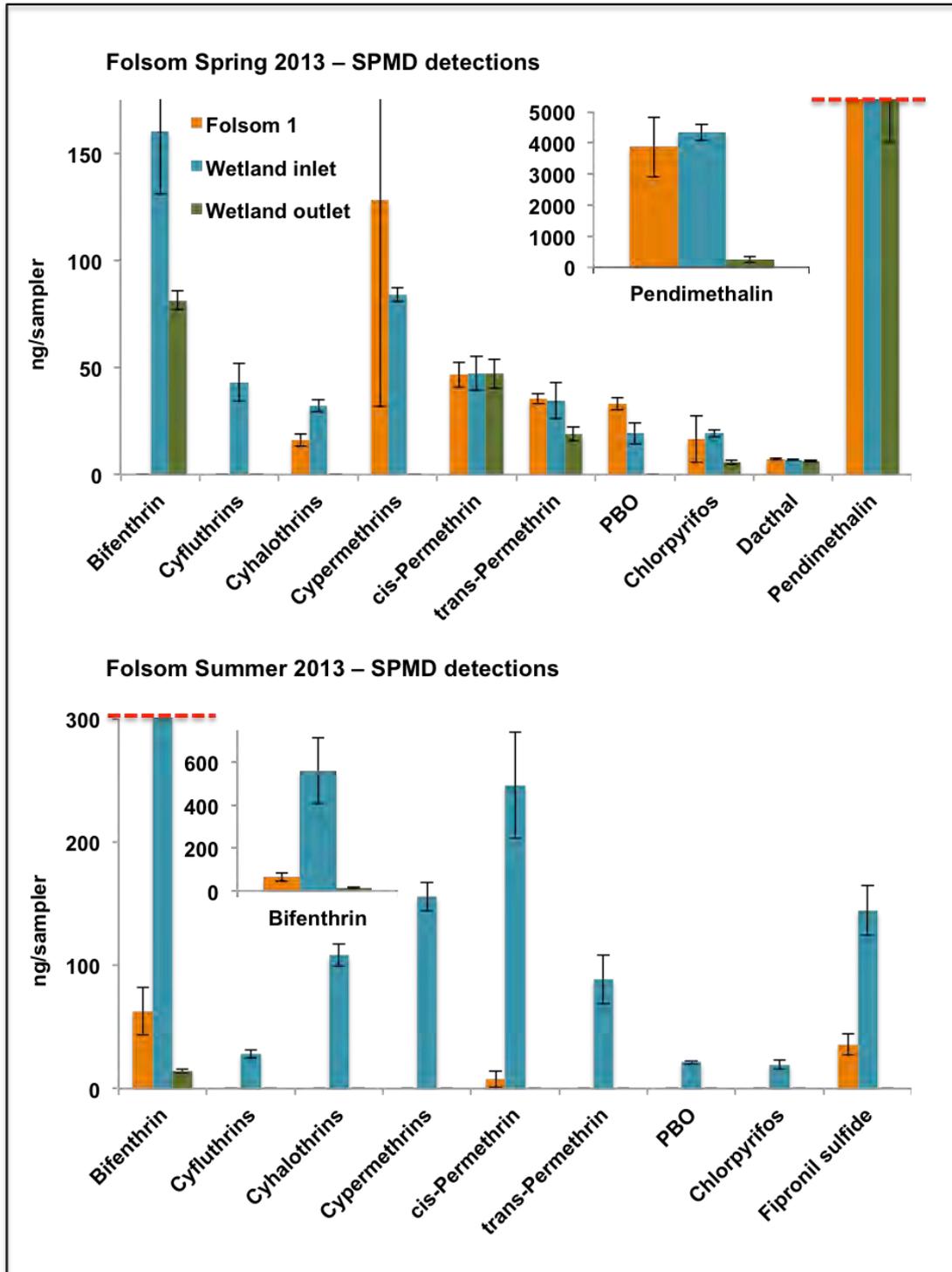
To better compare the wetland's inlet and outlet pesticide detections and to those of the Folsom 1 site, the data is reported and plotted by concentration (Figure 1S; Tables 1S and 2S; below). Five of eight pyrethroid insecticides (bifenthrin, cyfluthrin, cyhalothrin, cypermethrin and permethrin) were frequently detected in Folsom, while fenpropathrin, deltamethrin and esfenvalerate were not detected. As expected, the synergist additive PBO was typically detected in association with pyrethroid pesticides. Bifenthrin was generally the most dominant pyrethroid detected followed by *cis*-permethrin and cypermethrin.

The wetland screening revealed clear differences between the inlet and the outlet. The wetland inlet generally showed the highest number and magnitude of pesticide detections. Bifenthrin was halved by remediation through the wetland in spring and reduced from 561 ( $\pm 154$ ) to 14 ( $\pm 1.4$ ) ng/sampler in the summer. All other pesticides detected at the inlet in summer were reduced to below detection at the outlet. In the spring, permethrin slightly decreased from 82 ( $\pm 16$ ) to 66 ( $\pm 10$ ) ng/sampler, however there was no observed decrease in dacthal at the outlet. Chlorpyrifos was reduced to about a third, while pendimethalin was reduced from  $>4000$  ng/sampler at the inlet to 243 ( $\pm 88$ ) ng/sampler (166 ( $\pm 3.4$ ) to 34 ( $\pm 16$ ) ng/L in water grabs) at the outlet. It should be noted that the inlet generally exhibited slightly higher flow conditions, which may have increased sampling rates for the inlet compared to the outlet.

Hydrophobic pesticides were generally not detected in water which would have allowed verification of remediation success. The fipronils were detected in water and the data are not conclusively in support of remediation (Tables 1S and 2S; below). In fact, trends observed for fipronil sulfide by water grab contrasted those by SPMD in that concentrations increased through the wetland. It is possible that fipronil is degraded to the sulfide in the wetland. Overall, the findings of this screening effort are in support of wetland remediation of the pesticides analyzed.

SPMD-derived data for a constructed wetland support the effectiveness of wetlands in pesticide remediation. Sampler concentrations measured at the outlet were generally reduced if not completely removed compared to concentrations measured at the inlet. While these findings are promising, they should be interpreted with caution, as differing flow conditions between the inlet and outlet may have affected uptake in samplers.

**Figure 1S.** Comparison of pesticide detections in Folsom 1, wetland inlet and outlet in spring and summer 2013 using SPMD.



Only pesticides detected in SPMDs at one or more of the three sites are depicted. Each column represents the mean across 3 replicate samplers. Error bars represent standard deviation. The inserts show full-scale plots for off-axis compounds (red lines). Refer to Tables 1S and 2S for measured concentrations and non-detects of all target pesticides.

**Table 1S.** Summary of pesticide detections in water and SPMDs in Folsom 1 and the wetland during the spring deployment (Feb-Mar 2013).

Target pesticide	Target sampler	Fol 1 water freq. (%)	Fol 1 - SPMD (ng/sampler)	WLI – water (ng/L)	WLI - SPMD (ng/sampler)	WLO – water (ng/L)	WLO – SPMD (ng/sampler)
Diazinon	Both	0	ND	ND	ND	ND	ND
Fipronil	POCIS	80	ND	45 (4.2)	ND	47 (3.0)	ND
Fipronil desulfinyl	POCIS	60	ND	27 (1.5)	ND	28 (1.6)	ND
Fipronil sulfide	POCIS	0	ND	ND	ND	24 (0.9)	ND
Fipronil sulfone	POCIS	60	ND	103 (8.5)	ND	84 (11)	ND
Bifenthrin	SPMD	0	ND	ND	160 (29)	ND	81 (4.5)
Chlorpyrifos	SPMD	0	17 (11)	ND	19 (1.8)	ND	5.9 (1.1)
Cyfluthrin	SPMD	0	ND	ND	43 (8.9)	ND	ND
Cyhalothrin	SPMD	0	16 (2.8)	ND	32 (2.7)	ND	ND
Cypermethrin	SPMD	0	128 (96)	ND	84 (3.3)	ND	ND
Dacthal	SPMD	0	7.2 (0.3)	ND	6.9 (0.2)	ND	6.5 (0.4)
Deltamethrin	SPMD	0	ND	ND	ND	ND	ND
Esfenvalerate	SPMD	0	ND	ND	ND	ND	ND
Fenpropathrin	SPMD	0	ND	ND	ND	ND	ND
Metolachlor	SPMD	0	ND	ND	ND	ND	ND
Oxyfluorfen	SPMD	0	ND	ND	ND	ND	ND
PBO*	SPMD	40	33 (2.9)	ND	19 (5.2)	ND	ND
Pendimethalin	SPMD	80	3,866 (957)	166 (3.4)	4,330 (250)	34 (16)	243 (88)
Permethrin	SPMD	0	82 (8.3)	ND	82 (16)	ND	66 (10)
Prometryn	SPMD	0	ND	ND	ND	ND	ND
Propyzamide	SPMD	0	ND	ND	ND	ND	ND
Pyraclostrobin	SPMD	0	ND	ND	ND	ND	ND
Tebuconazole	SPMD	40	ND	ND	ND	ND	ND
Trifluralin	SPMD	0	ND	ND	ND	ND	ND

Water freq. refers to detection frequency of composite water samples collected at Folsom 1 throughout the sampler deployment ( $n=5$ ). D# denotes day of sampling. Water concentrations (mean  $\pm$  standard deviation) are given for the wetland inlet and outlet (WLI and WLO) based on grab samples collected on the last day of deployment (Day 28, three replicates per site). Sampler concentrations (mean  $\pm$  standard deviation) are given for D28 (3 replicate samplers). ND = non-detect ( $<$ reporting limit (6 ng/sampler) or  $<3x$  blank). SPMD compounds are highlighted in grey.

**Table 2S.** Summary of pesticide detections in water and SPMDs in Folsom 1 and the wetland during the summer deployment (July 2013).

Target pesticide	Target sampler	Fol 1 water freq. (%)	Fol 1 - SPMD (ng/sampler)	WLI – water (ng/L)	WLI - SPMD (ng/sampler)	WLO – water (ng/L)	WLO - SPMD (ng/sampler)
Diazinon	Both	0	ND	ND	ND	ND	ND
Fipronil	POCIS	55	ND	66 (3.6)	ND	17 (0.80)	ND
Fipronil desulfinyl	POCIS	9	ND	19 (0.80)	ND	15 (0.60)	ND
Fipronil sulfide	POCIS	0	36 (8.7)	8.3 (0.40)	145 (20)	16 (0.50)	ND
Fipronil sulfone	POCIS	100	ND	47 (1.3)	ND	29 (1.7)	ND
Bifenthrin	SPMD	0	63 (20)	18 (2.8)	561 (154)	ND	14 (1.4)
Chlorpyrifos	SPMD	0	ND	ND	19 (3.7)	ND	ND
Cyfluthrin	SPMD	0	ND	ND	28 (3.4)	ND	ND
Cyhalothrin	SPMD	0	ND	ND	114 (9.0)	ND	ND
Cypermethrin	SPMD	0	ND	ND	156 (11)	ND	ND
Dacthal	SPMD	0	ND	ND	ND	ND	ND
Deltamethrin	SPMD	0	ND	ND	ND	ND	ND
Esfenvalerate	SPMD	0	ND	ND	ND	ND	ND
Fenpropathrin	SPMD	0	ND	ND	ND	ND	ND
Metolachlor	SPMD	0	ND	ND	ND	ND	ND
Oxyfluorfen	SPMD	0	ND	ND	ND	ND	ND
PBO*	SPMD	0	ND	ND	21 (1.3)	ND	ND
Pendimethalin	SPMD	18	ND	6.8 (0.80)	ND	ND	ND
Permethrin	SPMD	18	ND	ND	334 (63)	ND	ND
Prometryn	SPMD	0	ND	ND	ND	ND	ND
Propyzamide	SPMD	0	ND	ND	ND	ND	ND
Pyraclostrobin	SPMD	0	ND	ND	ND	ND	ND
Tebuconazole	SPMD	9	ND	ND	ND	ND	ND
Trifluralin	SPMD	0	ND	ND	ND	ND	ND

Water freq. refers to detection frequency of composite water samples collected at Folsom 1 throughout the sampler deployment (n=5). D# denotes day of sampling. Water concentrations (mean ± standard deviation) are given for the wetland inlet and outlet (WLI and WLO) based on grab samples collected on the last day of deployment (Day 28, three replicates per site). Sampler concentrations (mean ± standard deviation) are given for D28 (3 replicate samplers). ND = non-detect (<reporting limit (6 ng/sampler) or <3x blank). POCIS target compounds screened for in SPMD are highlighted in grey.