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

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1.0 Background

Several studies have detected pesticides in California surface waters at concentrations that are above water quality benchmarks set for aquatic species (*e.g.*, Gan *et al.*, 2012; Starner and Goh 2012; Ensminger *et al.*, 2013). In particular, 2,4-D, triclopyr, bifenthrin, fipronil, diazinon, malathion and imidacloprid have been frequently detected in northern and southern California urban and agricultural sites (Starner and Goh 2012; Ensminger *et al.*, 2013). Monitoring studies rely heavily on grab sampling, which only provides a chemical concentration at one point in time (*i.e.*, time of sampling). A downfall with grab sampling is that pesticide pulses or peak inputs from changes in flow, runoff, or increased precipitation are often missed. Use of composite sampling has aided in capturing these changes, however like grab samples, peak inputs may be missed if the water is not continuously sampled over time. A matter of wrong timing can lead to 'false' non-detections and/or underestimation of exposure of some contaminants to non-target aquatic organisms. Another short-coming to traditional water sampling is that the truly dissolved fraction (*i.e.*, the fraction 'bioavailable' for organism uptake) cannot be accounted for. One way to overcome limitations of traditional water monitoring approaches is through the use of passive samplers, which enable integrative sampling of dissolved phase pesticides over time.

Passive samplers are semi-quantitative tools used to sample otherwise challenging trace contaminants from air, water and sediment. These samplers typically contain a sampling medium, specific for the contaminant(s) of interest, enclosed within a membrane(s). Only dissolved phase chemicals are available for uptake, thus samplers essentially mimic aquatic organism exposure. Various samplers have been developed, covering a range of chemicals that span across non-polar and polar pesticides. The semi-permeable membrane device (SPMD) was developed to detect non-polar chemicals (Huckins *et al.*, 1993). This sampler is based on the partitioning of chemicals between water and a lipid medium, which is intended to serve as a surrogate for fish fats. The polar organic chemical integrative sampler (POCIS), designed for polar compounds, contains a sorbent medium (Alvarez *et al.*, 2004), which takes up chemicals by adsorption.

Chemical uptake into passive samplers is dictated by the pesticide's physicochemical properties such as the octanol-water partition coefficient (K_{ow}). Pesticides applied in California range from polar pesticides such as imidacloprid with log K_{ow} of 0.33 to hydrophobic pesticides such as pyrethroids with log K_{ow} values up to nearly 7. It is not possible to cover such a wide range of pesticides with one sampler, thus utilizing the SPMD and POCIS together will allow coverage of a broad range of chemicals. As a general rule of thumb, the SPMD is considered to sample chemicals with log $K_{ow} > 3$, whereas the POCIS is intended for chemicals with log $K_{ow} < 3$. This may not always hold true, as it is difficult to predict the behavior of pesticides that border a log K_{ow} of 3. For these pesticides, determining the most appropriate sampler type is not always straightforward especially if the chemical has not previously been validated for the sampler in question. Some challenges of uptake into passive samplers include: 1) chemical crossing of the water boundary layer, 2) transport across the membrane, 3) transfer from the membrane to the sorbent or lipid medium and 4) sampler fouling (Harman *et al.,* 2012).

Passive samplers can be divided into two main groups: 'equilibrium' and non-equilibrium 'linear' samplers. Linear samplers, including the SPMD and POCIS, are designed for continuous uptake of chemicals over a given time. It is a prerequisite, however, that chemical uptake is in

the linear phase for the entire sampling period. When linearity is met, chemicals are taken up at a constant rate over time, and concentrations in the matrix and those extracted are linearly related (Zabiegala *et al.,* 2010). With typical deployment times of 28 days or longer, these devices are ideal tools to measure time-weighted average concentrations (TWA) of chemicals that may fluctuate over extended periods of time. The TWA can be determined from the sampling rate (*R*s), which is defined as the volume of water sampled per unit of time (*i.e.*, L/d); it is based on a linear uptake model. Only when the sampled water volume is known, can the accumulated chemical, in the sampler, be related to a water volume. Once the chemical mass and the sampled water volume are known, it is possible to determine a TWA in units of mass per volume (*e.g.*, ng/L).

Passive samplers are only quantitative when the *Rs* is known. Sampling rates are determined by laboratory calibration studies, where all parameters including chemical concentration, water velocity, temperature, *etc.*, are kept constant. In the field, however, *R*s will likely vary from those under laboratory conditions because water quality parameters fluctuate. High water velocity, for example, will increase *R*s, while fouling may impede uptake across the membrane, consequently decreasing *Rs*. The difficulty in determining field sampling rates represents one major limitation to passive samplers. *R*s for SPMDs generally exceed 1 liter per day (Huckins *et al.*, 1999), while POCIS sampling rates typically fall below 1 liter per day (Morin *et al.*, 2012). In other words, SPMDs can sample volumes in excess of 28 L per deployment improving detection of hydrophobic chemicals that are often present below the analytical detection limit in 1 L of water (*i.e.*, water grab sample). While POCIS sampling rates are lower than those for SPMDs, the continous uptake presents the opportunity to capture pulses of hydrophilic pesticides, which may be present in appreciable concentrations during peak runoff.

Performance reference compounds (PRCs) are compounds added to the SPMD sampler prior to deployment in order to determine their loss from the membrane over the sampling period. The PRC concept is based on the principle of isotropic exchange, during which the chemical exhange across the membrane is equal in both directions. Under this condition, changes in the chemical loss rate from the membrane due to variable environmental parameters such as water velocity or fouling will be equal to changes in uptake rates. In practice, the measured loss of the PRC, over the sampling period, can determine the field loss, which is then compared to the PRC loss under controlled laboratory conditions. From these losses, a correction factor can be determined and applied to the laboratory sampling rate for the target chemical in order to determine the field specific sampling rate; each field site requires its own *R*s. To achieve a reliable correction factor, the PRC loss must be at least 20%, but should not exceed 80%. The SPMD has been used extensively for sampling of polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs), and for these contaminant groups, PRCs exist (Huckins *et al.*, 2002). Booij *et al.,* (1998) showed that *R*s correlates well with log K_{ow} across a range of PCBs and PAHs. Compounds with similar log K_{ow} are thus considered to behave similarly in terms of uptake into the SPMD, and one PRC can act as surrogate for a range of chemicals with similar log K_{ow}. Compounds not expected to be present in the sampled water body should be selected as PRCs. Often, PRCs remain limited to PAH and PCB compounds, which have been applied as surrogate PRCs for other chemicals, such as pesticides. For pyrethroid insecticides (*e.g.,* bifenthrin), a lack of published calibration studies and PRC validation tests limit the confidence in using traditional PRCs for this compound group. Pyrethroids are structurally unique, exhibiting chemical

structures that deviate from other pesticides, PAHs and PCBs. It is thus questionable that the behavior of pyrethroid insecticides is directly comparable to that of other chemicals validated for SPMDs. Isotropic exchange into SPMDs has only been confirmed for chemicals known to be transported across the membrane via partitioning. Despite similarity in log K_{ow}, the surrogate PRC approach is only appropriate for pyrethroids if they are lost from the sampler at a similar rate as the surrogate PRC. While laboratory sampling rates have been determined for bifenthrin (O'Brien *et al.,* 2012), to our knowledge, no research has attempted to evaluate the usefulness of PCBs as PRCs for pyrethoid pesticides. SPMDs are quantitative under field conditions for compounds for which PRCs have been validated (Huckins *et al.*, 2002). However, when PRCs are not used and/or *R*s is not available, results can be be reported as a mass of chemical per sampler (*i.e.,* ng/SPMD). Although considered qualitative, these results are still valuable in determining relative amounts of chemicals at sampled field sites (Alvarez 2010).

Chemical uptake into POCIS does not occur by simple partitioning, and development of PRCs for POCIS has seen limited success. Until PRCs or an alternative methodology are available for POCIS, this sampler can only be used for quantitative purposes through labor-intensive site and chemical-specific calibration studies. Although POCIS reduce sample preparation by concentrating chemicals onto an easily extractable sorbent, there are some potential limitations. Vermeirssen *et al.,* (2012) have demonstrated that compounds accumulating within the POCIS membrane leads to uptake non-linearity and delayed uptake kinetics. The observed non-linearity has obvious implications for derivation of sampling rates using linear models. In addition, POCIS extraction methods use water and methanol, almost interchangeably, to rinse the sorbent from the membranes prior to extraction (Alvarez 2010). Only the chemical content accumulated in the sorbent is used to quantify the sampler concentration (and sampling rate). Rinsing with methanol has the potential to extract compounds from the membranes, thereby potentially overestimating the actual amount taken up in the sampler sorbent. This may lead to variability in sampling rates compared to studies employing a water rinse. However, with appropriate chemical and site-specific validation, this sampler has great potential as an applicable and practical screening tool.

To date, few studies have used passive samplers to measure pesticides under environmental conditions in California. Field-specific calibration data does not exist for POCIS in this region, thus the quantitative use of this sampler is limited. Moreover, research validating the use of PCB PRCs for pyrethroid sampling by SPMDs is not available. Very few comprehensive comparison studies have evaluated the use of passive samplers for water monitoring relative to traditional grab sampling (Coes *et al.,* 2014). Thus the current study is necessary for evaluating these sampler's applicability and usefulness in monitoring over an extended period of time.

Study Objectives

The overall objectives of this study were:

1. To evaluate the applicability of POCIS and SPMDs in measuring a broad range of target pesticides at environmentally relevant concentrations, as compared to grab sampling;
2. To extract samplers and analyze pesticides at environmentally relevant concentrations;

3. To monitor target analytes at one agricultural and two urban field sites;
4. To determine time-weighted average concentrations of each pesticide following deployment.

Study Components

This study consisted of the following components:

1. Preparation of sampling equipment for deployment at desired urban and agricultural sites;
2. Deployment of SPMDs and POCIS for 28 days;
3. Collection of water quality parameters such as water temperature;
4. Collection of samplers, pesticide extraction, chemical and data analysis.

In addition to the main tasks and objectives, an experiment was conducted to evaluate the possible retention of target pesticides in the POCIS membrane. This evaluation was achieved through extraction and analysis of pesticides in both POCIS membranes and sorbent. In addition, to evaluate the suitability of the PRC concept for pyrethroid insecticides, ^{13}C-labelled *cis*-permethrin was spiked into all SPMDs to test outward exchange of this compound across the membrane. As an additional study, the inlet and outlet of a constructed wetland, in Folsom, were monitored for pesticides to evaluate the pesticide removal efficiency through the wetland. Further information is provided in the Supplemental Material.

2.0 Materials and Methods

2.1 Chemicals, samplers and materials

This research covered a broad range of current-use pesticides spanning the log K_{ow} range from <1-7 (Table 1). The selected compounds include 16 insecticides, 16 herbicides, 5 fungicides, 5 degradation products and 1 synergist compound used as an additive in pesticide formulations. The selection was based on the California Department of Pesticide Regulation's (CPDR) crop reports for Monterey County and online databases for urban pesticide usage in Sacramento County (http://www.cdpr.ca.gov/docs/pur/purmain.htm). Bifenthrin, diazinon, fipronil, fipronil sulfide and sulfone were purchased from ChemService (West Chester, PA, USA). Fipronil amide and desulfinyl were provided *gratis* by the U.S. EPA chemical repository. ^{13}C-labelled *cis*-permethrin (for evaluation as PRC) was purchased from Cambridge Isotope Laboratories (Tewksbury, MA, USA). The remaining chemicals listed in Table 1, including surrogate standards (barban and alachlor) and internal standards (d_{10}-phenanthrene, d_{12}-chrysene, d_{12}-perylene and monuron), were purchased from Sigma Aldrich (St. Louis, MO, USA).

Standard size SPMDs (96 cm x 2.5 cm), containing ultra-high purity triolein (spiked with ^{13}C-*cis*-permethrin), and POCIS (with 0.2 ± 0.05 mg HLB) were purchased from Environmental Sampling Technologies (EST; St. Louis, MO, USA; Appendices 1 and 2).

For solid-phase extraction (SPE) of water and POCIS samples, Oasis HLB SPE (6 cc, 500 mg) and empty cartridges (6 cc) plus frits were purchased from Waters (Milford, MA, USA). EnviCarb SPE cartridges (6 cc, 500 mg, Supelco) with graphitized carbon for clean-up of SPMDs were obtained from Sigma Aldrich. Solvents were of HPLC or higher grade. Sodium sulfate for drying of extracts was obtained from Sigma Aldrich and baked at 450°C before use. All glassware was baked at 450°C and rinsed with dichloromethane before use.

2.2 Laboratory specific POCIS calibration

POCIS were calibrated to determine sampling rates under a controlled static renewal design. Samplers were placed into a circular fiber-glass tank (120 L tap water, 19°C, 28 d; Appendix 3) and spiked at a nominal concentration of 2 ug/L of the hydrophilic pesticides of interest (Table 1). Thirty POCIS were placed into the tank and a lid was placed on the top to limit light exposure and evaporation. Spike renewals were made every 3 to 4 days and each renewal involved transferring the samplers to another tank with fresh exposure water. Triplicate water grab samples (1 L) were collected before and after renewals and triplicate POCIS were removed at ten time points (1, 3, 5, 7, 10, 14, 17, 21, 24 and 28 days) to evaluate linearity of uptake. A control tank, containing three POCIS in tap water, was run alongside the calibration, while field blanks were exposed to the air during each sampling/renewal.

Three SPMDs were included to monitor the loss of ^{13}C-labelled *cis*-permethrin, which had been spiked into SPMDs for evaluation as a PRC. SPMDs were collected at the end of the experiment for analysis.

2.3 Field Sites and deployments

One urban (Folsom, CA, referred to as Folsom 1; Appendix 4) and one agricultural (Salinas, CA; Appendix 5) field site located in Sacramento and Monterey counties (Northern California), respectively, were selected for this study. Both types of passive samplers were deployed at both sites in the spring, summer and fall of 2013.

Field calibrations were conducted to determine field-specific sampling rates for POCIS target pesticides. Calibrations were held during the summer months at both locations. In these experiments, 30 POCIS and 3 SPMDs were deployed for 28 days. In order to determine POCIS sampling rates under non-constant field conditions, it is necessary to know the TWA water concentration for each pesticide for the entire deployment period. To this end, an ISCO 6700 auto-sampler was set up at each site to take hourly water samples (40-150 mL each, depending on the length of sampling (1 - 4 days)). A 4 L clean amber glass bottle was used as the collection bottle and kept cold by icepacks inside of the ISCO. Composite water samples (1 L) were collected in triplicate at least twice a week, when the bottle and ice were exchanged. POCIS and water were sampled in triplicate at ten time points (1, 3, 5, 7, 10, 14, 17, 21, 24 and 28 days), whereas SPMDs were collected at the end of the experiment.

To compare pesticide detection efficiency of samplers and grab sampling additional deployments were conducted during the spring and fall at both locations. These experiments included deployment of three POCIS and three SPMDs. Field blanks, for each sampler type, as appropriate were exposed to the atmosphere during sample deployments and retrievals. Water samples (1 L; glass amber bottles) were collected by grab in triplicate, once per week from test

initiation until termination (5 times total), whereas samplers were only collected at test termination (day 28); samplers were gently cleaned every week during deployment to remove fouling.

2.4 Water extractions

Water samples were extracted following a protocol adapted from Hladik *et al.*, 2008. Samples were extracted within 3 days of collection and a procedural blank was prepared with each batch of 3-6 samples. Samples (1 L) were filtered through Whatman glass microfiber filters (0.7 µm pore-size) prior to extraction and surrogate standards were added to each sample and blank (Section 2.6). Samples were extracted using Oasis® HLB SPE cartridges (6cc, 500mg) that were preconditioned with methanol, ethyl acetate and de-ionized (DI) water prior to sample addition. Water samples were run through the cartridges at a rate of approximately 10 mL/min. Following sample addition, cartridges were covered with cleaned aluminum foil (rinsed with dichloromethane) to avoid contamination from the surrounding atmosphere and dried for 1 hour to remove any residual water. Drying was achieved by opening the cartridges under vacuum to run ambient air through. Compounds were then eluted with ethyl acetate (2 column volumes) into test tubes. Sample bottles were rinsed with dichloromethane and the rinsate was dried through pre-baked anhydrous sodium sulfate and combined with the SPE extracts. Extracts were concentrated to 1 mL and split in two for analysis by liquid and gas chromatography with mass spectrometry detection (LC-MS/MS and GC-MS, respectively). Extracts were further concentrated to 100 µL, and samples for LC-MS/MS were solvent exchanged into acetonitrile.

2.5 POCIS and SPMD processing

Following retrieval, individual samplers were subjected to exterior cleaning to remove any topical debris. The samplers were individually wrapped in solvent rinsed aluminum foil, transported on ice to the laboratory and stored (-20°C) until extracted.

2.5.1 POCIS extraction

POCIS membranes were removed (cut) from the center of the sampler and the HLB sorbent was rinsed with water into an empty SPE cartridge (6 mL), containing a frit. The sorbent was spiked with surrogate standards, a second frit was placed on top and the sorbent was dried for 30 min. Each sample was eluted with 40 mL of methanol, concentrated to 2 mL, split in two for instrumental analysis and each half was concentrated further to 100 µL. Samples for LC-MS/MS were solvent exchanged into acetonitrile. Prior to analysis, internal standards were added (Section 2.6).

POCIS membranes, from the lab calibration experiment, were extracted to evaluate possible pesticide accumulation, *i.e.*, to assess possible non-linearity and delayed uptake kinetics. Membranes were placed in cleaned glassed beakers, surrogate standards were added with 15 mL methanol and beakers were placed on a shaker (50-60 rounds per minute for 30 mins). The extraction was repeated with another 15 mL of methanol, the two extracts were combined and reduced under nitrogen to 0.2-0.4 mL. The membrane extracts were transferred to HLB SPE cartridges and target compounds were eluted, reduced and prepared for analysis using the same protocol as for the water samples (Section 2.4).

2.5.2 SPMD extraction and clean-up
SPMD samples and field blanks underwent a 4-step extraction and clean-up procedure including pre-cleaning, dialysis, liquid-liquid extraction (LLE) and SPE clean-up as outlined below.

SPMDs were pre-cleaned according to Huckins *et al.*, 2006. In brief, pre-cleaning included a hexane rinse, rubbing under running water, followed by separate rinses in hydrochloric acid, water, acetone and finally in isopropyl alcohol.

SPMD dialysis followed procedures provided by EST (EST 2013) with slight modifications. Pre-cleaned individual SPMDs were placed into clean mason jars. Hexane (150 mL) plus surrogate (alachlor) were added and samples were incubated at 19°C in the dark. After 24 hours, each membrane was placed into a new clean mason jar, 150 mL of hexane and surrogate were added to each jar and membranes were incubated once more (19°C, 24 h, dark). In the meantime, the first hexane extract was stored in the fridge. After the second incubation, the two hexane extracts were combined and the volume was reduced using a rotary evaporator, followed by nitrogen (N_2) blow down to approximately 1 mL. (A third dialysis resulted in <5 % additional recovery of extraction and increased matrix effects. Unreported preliminary data).

LLE was conducted to remove triolein from the SPMD extracts. An acetonitrile: hexane LLE method was adapted from Esteve-Turrillas *et al.,* (2006). Each sample was transferred to a clean 30 mL glass separatory funnel and topped with 5 mL hexane pre-saturated with acetonitrile. The sample was extracted three times with 5 mL acetonitrile pre-saturated with hexane in order to separate small amounts of the triolein while partitioning the pesticides into the acetonitrile phase. Each extraction included a 2 min shake followed by a 10-15 min separation period. The acetonitrile extracts were reduced to approximately 1 mL by rotary evaporator, transferred with dichloromethane to test tubes through pre-baked sodium sulfate and reduced to a small volume (100-200 µL) by nitrogen (N_2) blow down. The extract fully exchanged to dichloromethane was ready for SPE clean-up.

SPMD extracts were further cleaned using EnviCarb graphitized carbon SPE cartridges (6 cc, 500 mg). Cartridges were pre-conditioned with dichloromethane before the sample was loaded and were eluted with 10 mL dichloromethane at approximately 10 mL/min. Each extract was solvent exchanged to ethyl acetate, concentrated to 240 µL and spiked with an internal standard for GC-MS analysis (Section 2.6.2).

2.6 Instrumental analysis
The selected pesticides include both GC and LC-amenable compounds. Water and POCIS extracts were analyzed by LC-MS/MS and GC-MS, while SPMD extracts were analyzed by GC-MS. Internal standards were added prior to analysis (monuron for LC-MS/MS and d_{12}-chrysene and d_{12}-perylene for GC-MS). Calibration standard solutions were prepared using stock standards; an external calibration curve was used.

2.6.1 LC-MS/MS analysis
To maximize sensitivity of the LC-MS/MS, optimization of each compound was performed via infusion. Briefly, each compound was infused into the MS at 1 mg/L in a water: acetonitrile

(50:50) solution. The following parameters were optimized for each compound: declustering potential (DP), entrance potential (EP), collision energy (CE), collision cell exit potential (CXP) and focusing potential (FP).

Chromatographic separation was performed on an Agilent 1100 series liquid chromatography system (Agilent Technologies, Santa Clara, CA, USA) equipped with a quaternary pump and auto sampler. The analytical column was a Titan RP-C18 (100mm x 2.1mm, 3µm) coupled with a Pursuit C18 MetaGuard guard column (3µm, 4.6mm; Agilent Technologies, Santa Clara, CA, USA). Gradient elution (95% A to 5% A in 30 min, re-equilibration was 3 min) was used to separate each compound with water (0.1% acetic acid; mobile phase A) and acetonitrile (mobile phase B). The flow rate was 0.3 mL/min and 5µL of each sample was injected. The LC was coupled to a mass spectrometer (Ab Sciex, Framingham, MA, USA) containing an ESI as the ionization source and triple quadrupole as the mass analyzer. Data acquisition was performed in MS/MS using monitored reaction mode (MRM). Data acquisition and processing were completed using Analyst software (Applied Biosystems; Grand Island, NY, USA).

Mass transitions for each analyte are provided in Appendix 6.

2.6.2 GC-MS analysis

GC-MS analysis was performed on an Agilent 6980/5973 system equipped with an autosampler, and using a DB-5ms column (30 m x 0.25 mm ID x 0.25 µm film). The analytical method was adapted from previously published methods for mixed pesticides and pyrethroids (Hladik *et al.*, 2008 and 2009).

All samples were made up to volume prior to analysis, when calibration standards (0.025 – 2.5 ng/µL) were also made up. At that time, internal standards (IS) were added to all samples and standards, and an instrument blank was made that contained IS and solvent only. The instrument blank, samples and standards all contained the same amount of IS, which was used to monitor instrument performance throughout each run. The final volume of all samples was 120 µL, with the exception of samples from the lab calibration study, which led to final samples of 1 mL.

Each batch of roughly 20 samples was preceded by the instrument blank and 10 calibration standards, and an intermediate calibration standard was inserted between every 10 samples and again at the end of the run. The instrument was calibrated by external standards using two 5-point calibration curves; one for the low concentration range and one for the high concentration range. Matrix spikes were included to account for matrix effects. For analysis of POCIS and water, matrix spikes were completed by spiking and re-injecting 3 samples (at low, medium and high concentration) post first injection. For SPMDs, blank samplers were extracted to produce a full calibration range from matrix spikes (method matrix spikes compared well with matrix spiked environmental samples).

Samples (2 µL) were injected in pulsed splitless mode with an injector temperature of 275°C and a 0.9 min pressure pulse of 50 psi. Helium was used as carrier gas with a flow of 1.2 mL/min. The GC oven was heated to 80°C, held for 1 min, where after the temperature was ramped at 10°C/min until 300°C, where it was held for 10 min. The MS transfer line heater, quadropole and ion source were heated to 280, 150 and 230°C, respectively. The MS was operated in electron

ionization mode and data were collected by selected ion monitoring (SIM) after a 5 min solvent delay.

The SIM method was developed through full scan analysis of individual compounds for selection of retention time windows, quantifying and qualifying ions (Appendix 7). The SIM program used a dwell time of 50 msec and included 21 compound groups. To avoid column degradation from matrix addition, the column was trimmed (10 cm) after each run of roughly 20 environmental samples. After column maintenance, the SIM program was checked and retention time windows were adjusted accordingly.

2.7 TWA calculation

Pesticide time-weighted average (TWA) concentrations were calculated from measured water concentrations using the following equation:

$$\mathrm{TWA} = \frac{t_1C_1 + t_2C_2 + \ldots + t_n}{t_1 + t_2 + \ldots + t_n}$$

where t is the time passed between the first and the second concentration measurement of a known time period and C is the average of the measured concentrations at the start and end of that time period. This calculation allows an overall dissolved phase concentration to be estimated during a known exposure time.

2.8 Rs calculation

The sampling rates of either laboratory or field calibrated POCIS compounds were quantified from the experimental data. If linearity is obeyed, the amount of pesticide in the sampler (C_s; in ng) is described by the following equation:

$$C_s = R_s C_w t$$

where R_s is the sampling rate (L/ day), C_w is the concentration of the compound in water (ng/L) and t is the exposure time (day).

*R*s can also be expressed via the concentration factor (CF, Tran *et al.*, 2007), which describes the sampled concentration (C_s) relative to the water concentration:

$$CF = C_s/C_w t = R_s$$

CF provides a C_w-normalized sampling rate, which is particularly useful for scenarios of fluctuating water concentrations (*i.e.*, field conditions). The CF approach was used in the present work for the lab calibration of the low K_{ow} pesticides, and for the field calibrations. An additional advantage of the CF approach is that the sampled volume (y-axis) can be read directly from the uptake curve at any given time (x-axis).

3.0 Results and Discussion

3.1 POCIS laboratory calibration

3.1.1 Measured water concentrations

POCIS were calibrated in the laboratory using tap water fortified with POCIS target pesticides (Table 1); the water solubilities of the investigated pesticides exceed the applied spike concentration of 2 µg/L. Yet, for many pesticides, the measured water concentrations were much lower than the nominal spike concentration and fluctuated throughout the experiment (Appendices 8a and 8b). It was expected that true chemical concentrations would be lower than nominal concentrations and that they would decline between renewals, mainly due to adsorption to container walls. Evaporation and photolytic degradation were not expected to occur as the exposure containers were covered to minimize such breakdown. Microbial degradation was not expected to occur in chlorinated tap water, however interference between pesticides and co-occurring water components could not be ruled out. Finally, pH may have affected both water solubility and sampler uptake for some compounds, however it is unclear if that resulted here. The data revealed no clear picture as to why the concentrations fluctuated.

Diazinon and fipronil were often measured below the reporting limit of 6 ng/L (Appendices 8a and 8b) and may partly be explained by their higher K_{ow}s when compared to the other POCIS compounds (Table 1). For carbaryl losses occurred between renewals, whereas other pesticides (*e.g.*, oryzalin), had higher water concentrations between renewals than immediately after spiking. Triclopyr, however, supports a time-dependent decline in spike concentration through the experiment. Although it was detected on D28 (~0.1 µg/L), it declined to non-detectable levels by D21. Additionally, concentrations of the fipronil degradates decreased from the D17 spike onwards and oddly, MCPA was only detected on D14. Overall, the concentrations of many pesticides fluctuated in a seemingly random manner during this experiment. It is unlikely that the added amount of pesticides differed between spikes as the same spike solution was used throughout the 28-day experiment. With no consistent trend identified, the most plausible explanation for the observed variability in water concentrations is that the spike solution (1 L) was not fully mixed into the experimental solution (120 L) prior to water collection. In consideration of the experimental static (no flow) conditions and the large volume of water used, it is possible that the manual mixing method was insufficient to produce a fully homogeneous solution. The water sampled may not reflect the true average concentrations of the entire solution, although three samples were collected for each sampling time. Furthermore, inhomogeneous mixing may have affected uptake into POCIS, and the calibration results should be viewed in this light.

3.1.2 POCIS sampling rates

POCIS calibration was conducted under static conditions to represent a "slowest uptake" scenario corresponding to quiescent field conditions, when diffusion across the membrane is expected to be slow. Alvarez *et al.,* (2004) note that the aqueous boundary layer influences analyte uptake, as otherwise diffusion would be relatively constant. Tran *et al.,* (2007) also state that because the aqueous membrane controls analyte uptake, uptake rates increase when the water becomes more turbulent. Membrane control was further demonstrated by Vermeirssen *et al.*, (2012), who observed an uptake lag phase for diazinon and diuron, which were also assessed

in the current study. Here, ten compounds with log K_{ow} above 3 (chlorothalonil, OH-chlorothalonil, diazinon, fipronil, MCPA and oryzalin; Table 1), ten compounds with log K_{ow} 2 – 3 (2,4-D, azoxystrobin, boscalid, carbaryl, diuron, malathion, myclobutanil, prometon, simazine and triclopyr) and three compounds with log K_{ow} below 1 (dimethoate, imidacloprid and methomyl) were tested in POCIS. All POCIS sorbent concentrations are presented in Appendix 9. Sampling rates and lag phases are listed in Table 2.

Compounds with a log K_{ow} >3

Compounds with a log K_{ow} *>3* were expected to accumulate strongly in the POCIS membrane. This hypothesis is well supported by the measured data (Fig. 1a-c), which revealed high discrepancies between standard sampling rates (*R*s, sorbent only) and those determined from the combined accumulation in sorbent and membrane (Rs_{tot}). Rs_{tot} is approximately twice the measured *R*s for diazinon, fipronil and fipronil degradates and as much as an order of magnitude higher than *R*s for oryzalin (Table 2).

Due to the fluctuating water concentrations for these compounds, sampling rates were best modeled using the concentration factor (CF) approach (Section 2.8). The value of normalizing concentration is best demonstrated for diazinon, fipronil and fipronil amide, for which the standard (non-CF) uptake plots indicate a plateau in the last half of the experiment (i.e., violation of linearity; Fig. 1a, left panel). In contrast, the CF-based uptake curves demonstrate linearity over most of the uptake period after the initial lag phase is overcome (Fig. 1a, right panel). The linearity of C_w-normalized data supports i) that POCIS sampling rates are independent of water concentration and ii) that the measured water concentrations are valid, despite the observed fluctuations and deviation from the nominal spike concentration. The comparatively high CFs calculated for fipronil amide on days 1 and 3 could indicate, however, that water concentrations, for this compound, were underestimated on these days (Fig. 1a).

Lag phases were evident for all compounds with a log K_{ow} *>3,* with the exception of MCPA, whose solubility is greater and log K_{ow} is less than the other compounds. Linear regression of the CF-curves enabled lag phase predictions for most compounds (Fig. 1a-c). The longest lag phases of 7.5 and 8.1 days were observed for OH-chlorothalonil and oryzalin, respectively. Both compounds were under strong membrane control in the first week, and oryzalin through the entire 28-day uptake (Fig. 1b, Table 2). Concentration normalization did not correct for a reduction in oryzalin's uptake. Diazinon began accumulating in the sorbent after a lag phase of 4 days, which is within the range observed by Vermeirssen *et al*., (2012). Similar lag phases were determined for fipronil sulfide and sulfone, while fipronil and fipronil desulfinyl exhibited lag phases of 0.7 and 2.4 days, respectively. A negative lag phase was determined for fipronil amide but this is likely an artifact of the seemingly underestimated water concentrations for the first 3 days of the experiment.

The data for chlorothalonil, OH-chlorothalonil and MCPA do not provide clear trends (Fig. 1c). Chlorothalonil was detected in water throughout the experiment; however it was sporadically detected in the membranes while not being detected in the POCIS sorbent at all. Analytical challenges may partly explain the lack of chlorothalonil detections. Contrasting these findings, Charlestra *et al.,* (2012) observed linear uptake of chlorothalonil in POCIS during 28 days under quiescent and flow conditions in both natural and synthesized river water, as well as in organic

matter-amended tap water. The hydrolysis product was detected in water from D5 to D17, thus possibly explaining the measured lag phase of roughly 5 days. POCIS detections of OH-chlorothalonil did peak by D21, however measured concentrations dropped to roughly D10 levels by the end of the experiment - membrane retention occurred during the first week but declined to concentrations near the detection limit. Manual calculation of the sampling rate resulted in a *R*s for OH-chlorothalonil of 0.23 L/d, based on an exposure length of 21 days – this is the highest *R*s determined for any compound tested in the lab calibration.

MCPA was not retained in the membrane, however a small sorbent peak on D1 was observed. This detection represents a so-called 'burst effect', which can occur during the initial wetting of the sorbent and membranes, and may be prevented by presoaking the samplers before deployment (Alvarez *et al.,* 2007); samplers were presoaked prior to the current experiment. Belles *et al.,* (2014) proposed that some compounds are under the control of diffusion into the sorbent's pores, an adsorption process called intraparticulate diffusion. This process may control the accumulation within POCIS when compared to membrane control.

POCIS uptake was relatively linear during the first two weeks, but highly variable (also within replicates) during the second half of the experiment. Tran *et al.,* (2007) obtained a curvilinear fit for MCPA in Empore disks (styrenedivinylbenzene copolymer sorbent) also with drop in MCPA concentrations from D15 to D21. These authors demonstrated isotropic uptake/release kinetics for triclopyr and suggested that other phenoxy herbicides such as MCPA and 2,4-D may exhibit similar release behavior. If MCPA is released in a similar manner from POCIS, loss could have exceeded uptake on days of low or no MCPA availability in the exposure water (App. 8a and b), such loss could explain the observed uptake pattern. As MCPA was only detected in water a couple of times, it is not possible to complete the modeling for this compound. (2,4-D exhibited similar behavior as MCPA, while triclopyr was relatively linear to the end of the experiment. Triclopyr and 2,4-D are discussed with the compounds having a *log* K_{ow} *2-3*).

The sampling rates determined for compounds with a log K_{ow} *>3* are relatively low. The data presented for chlorothalonil, its hydrolysis product and MCPA should be considered tentative. The sampling rate determined for diazinon, after 24 days (0.054 L/d), compares well with the *R*s determined under static conditions by Alvarez *et al.,* (2000; 0.056 L/d), however it is roughly four times lower than previous estimates under flow conditions (Thomatou *et al.*, 2011; Vermeirssen *et al.*, 2012). To our knowledge, no POCIS-PHARM (tri-phasic sorbent phase) sampling rates are available for fipronil and oryzalin for comparison with the current study. Recently, fipronil was calibrated in POCIS (HLB sorbent) under stirred conditions, resulting in linear uptake until 21 (of 28 days) and a sampling rate of 0.17 L/d (Thomatou *et al.*, 2015), compared to 0.059 L/d in the current study. A direct comparison is impossible due to the different sorbents and flow conditions used. The sampling rate of oryzalin (0.0050 L/d) was an order of magnitude lower than the other compounds. The comparatively low *R*s may be attributed to the particularly strong membrane retention observed. Indeed, Rs_{tot} for oryzalin (0.083 L/d) was higher than any of the other compounds, except for OH-chlorothalonil (0.083 L/d). The data obtained for fipronil, fipronil amide and fipronil desulfinyl did, however, produce linear curves for sound determination of *R*s, which may be useful to quantify TWA for these compounds under similar conditions. Lag phases were observed for many of the log K_{ow} >3 compounds, thus POCIS appears to be more of qualitative tool for such compounds.

Compounds with a log K_{ow} 2-3

Strong membrane retention and long lag phases were observed for many of the tested compounds with a log K_{ow} 2-3 (Fig. 2a-c, App. 9, Table 1). For pesticides in this category, sorbent concentrations peaked between D17 and D24, whereas membrane concentrations increased linearly throughout the 28-day experiment for majority of the pesticides. Unfortunately, the loss of sorbent-adsorbed contaminant, after the concentrations peaked, could not be explained by the measured water concentrations. It was expected that these compounds would exhibit higher sampling rates than those compounds with a log K_{ow} >3, however, *R*s for most compounds with a log K_{ow} 2-3 were an order of magnitude lower.

For azoxystrobin, boscalid, diuron and simazine (Fig. 2a), membrane accumulation dominated, resulting in Rs_{tot} ten-fold higher than standard *R*s (Table 2). It should be considered that *R*s and Rs_{tot} for these compounds were determined at D17, when the sorbent concentration peaked. The difference in sampling rates would be even higher if determined at D28, because membrane concentrations increased linearly until D28, whereas sorbent concentrations declined. *R*s were an order of magnitude lower than those for compounds with a log K_{ow} >3, except oryzalin. Due to the high membrane contributions to the total sampler content, Rs_{tot} were in the same range as those determined for the compounds with a log K_{ow} >3. Long lag phases from 5.2 to 7.6 days were observed for azoxystrobin, boscalid and diuron, while simazine accumulated in both membranes and sorbent from Day 1.

Ibrahim *et al.,* (2013) determined *R*s for axozystrobin, diuron, simazine and others using a flowing water design of similar volume to the current study and applied a water rinse to recover the sorbent from the samplers. Likely a result of the applied water flow, they determined much higher *R*s (0.15 to 0.26 L/d) for these pesticides than obtained in the current no-flow study (0.0030 to 0.0049 L/d; Table 2). Ibrahim's values compare well with data published for tap water (*e.g.*, Lissalde *et al.*, 2011). Ibrahim *et al.*,(2013) observed linear uptake of azoxystrobin from D0 to D21 (the length of the test) with no indication of a lag phase, but the latter cannot be verified as these authors did not investigate uptake prior to D5.

Carbaryl was not detected in appreciable concentrations in sorbent until 14 days of exposure, but the long lag phase could not be explained by membrane retention (Fig. 2b). Sorbent data are highly variable peaking on D21 with a low *R*s of 0.0014 L/d, contrasting findings of Lissalde *et al.*, 2011 (*R*s = 0.24 L/d) and Poulier *et al.*, 2015 (*R*s = 0.17 L/d, 14 d exposure). Myclobutanil and prometon uptake were linear until days 21 and 17, respectively (Fig. 2b). Lag phases were not observed for myclobutanil, while prometon exhibited a burst effect. Prometon and myclobutanil sampling rates are relatively high (0.0083 and 0.010 L/d, respectively) compared to the other compounds with a log K_{ow} 2-3.

The data for 2,4-D, triclopyr and malathion did not allow modeling of *R*s (Fig. 2c). The trends observed for 2,4-D are very similar to those of MCPA (both phenoxy herbicides). 2,4-D was not detected in the water or membranes on any day of the experiment, however the sorbent data indicates a burst effect and are highly variable across the last half of the experiment. The maximum accumulated amount measured on day 21 is relatively low at 114 ng/sampler, again similar to MCPA (App. 9). Tran *et al.* (2007) found 2,4-D, MCPA and triclopyr to exhibit

similar (curvilinear) uptake trends and to be sampled at lower rates than the other pesticides tested. The observed difference was attributed to the ionic forms of the phenoxy acids at neutral pH. Triclopyr uptake trends of the present study did not follow those of 2,4-D and MCPA. Uptake was somewhat linear thru D28 after a lag phase of roughly 4.8 days, but sorbent and membrane data fluctuated through the experiment; triclopyr was not detected in sorbent on D17. A *R*s of 0.035 L/d was calculated from the maximum accumulated amount of D24 which is comparatively high for the present study, but should be considered tentative.

Malathion was randomly detected in sorbent and membranes; sorbent detections occurred between 17 and 24 days of uptake. Water concentrations fluctuated, but not sufficiently to explain the lack of uptake in samplers. Belles *et al.*, (2014) derived a *R*s for malathion in POCIS-PHARM (tri-phasic sorbent) of 0.08 L/d, which represented the lower range of *R*s for that study, while Thomatou *et al.,* (2011) determined a *R*s of 0.31 L/d in POCIS (HLB sorbent).

Due to the strong membrane retention and lag phases observed, POCIS appears to be suitable as a qualitative tool for compounds within a log K_{ow} range of 2-3. Furthermore, as some sorbent concentrations dropped considerably after the peak, a two to three week deployment period may be more suitable rather than four weeks. Of the compounds tested here, the *R*s for simazine, myclobutanil and prometon may be valid for quantitative purposes, but only for the linear uptake periods observed (0 to 17 or 21 days). It should be considered that the sampling rates obtained in the present study are 1 to 2 orders of magnitude lower than published rates.

Compounds with a log K_{ow} < 1

Dimethoate was detected in sorbent after a 5 day lag phase (Fig. 3). Data variability prohibits identification of a trend, but pesticide uptake seems to have quickly reached a plateau, followed by a drop in sorbent concentration between days 17 and 28. Membrane concentrations followed sorbent concentrations, but remained at the plateau. Methomyl was taken up in sorbent from day 1 (*i.e.,* no lag phase), but immediately thereafter reached steady state (Fig. 3). Some sorbent samples had increased methomyl content on days 21-28, but data are inconsistent and were excluded from further analysis. Membrane/sorbent ratios varied through the experiment with higher relative membrane contribution with extended exposure. *R*s cannot be obtained for dimethoate or methomyl due to observed steady state conditions. Lissalde *et al.,* (2011) derived a *R*s of 0.17 and 0.087 L/d for dimethoate and methomyl, respectively during a 24 day exposure, whereas Poulier *et al.,* (2015) obtained a similar *R*s for dimethoate of 0.16 L/d, but only examined uptake for 14 days.

Data for imidacloprid also indicates a burst effect (Fig. 3). Sorbent and membrane contents overlapped and both increased linearly until D17. Sorbent concentrations decreased after D24 to levels as low as those measured by D5. Membrane concentrations continued to increase linearly throughout the experiment. The *R*s determined for imidacloprid (0.014 L/d; Table 2) is somewhat lower compared to compounds with a log K_{ow} >3, an order of magnitude higher than compounds with those with a log K_{ow} 2-3, and four times lower than that (0.06 L/d) determined by Belles *et al.,* (2014).

3.1.3 Summary of POCIS lab calibration

The sampling rates generated in the lab calibration should be considered tentative due to high data variability, fluctuating water concentrations, analytical non-detections and discrepancies with previously published data. Nevertheless, the data obtained from this experiment support the use of POCIS as a qualitative tool. Hydrophobic (*log* K_{ow}>3) and borderline hydrophobic (*log* K_{ow}> 2-3) compounds generally exhibited strong membrane retention and long lag phases, while hydrophilic compounds (methomyl and dimethoate) reached a plateau early in the uptake phase - all of which are in violation of linearity. Sampler accumulation of fipronil and two of its degradation products did follow linear uptake kinetics through the experiment, leading to sampling rates between 0.04 and 0.07 L/d that may be used for quantitative purposes, provided that similar experimental (quiescent) conditions govern.

POCIS sampling rates are independent of concentration (Tran *et al.*, 2007). Characterization of membrane control is important for quantitative studies using POCIS. For chemicals that exhibit long delays in uptake, the standard one-compartment linear model normally used for POCIS may not accurately describe POCIS uptake. Other researchers have used curvilinear or other models (*e.g.*, Tran *et al*., 2007; Ibrahim *et al.*, 2013), but it is challenging to model uptake of compounds with substantial delay in uptake. For such compounds, it is not possible to assure that pulses occurring in the first period of field deployment were captured. If sampling rates are not constant during an entire deployment, no single sampling rate can predict the true time-weighted average water concentration of a contaminant. It is recommended that calibration studies include sampling points early in exposure to detect potential lag phases.

The observed disparity between sampling rates determined using pesticide concentrations measured in sorbent only and those using the combined sorbent/membrane amount clearly highlights the importance of sample preparation. If methanol is used to rinse the sorbent off the membranes, chemical accumulated in the membrane is likely to be co-extracted in the rinse. The contribution of such membrane rinse cannot be assessed from the present study, but complete membrane extraction resulted in a doubling up to ten-fold magnification of the estimated sampling rates for the majority of the tested compounds. Vermeirssen *et al.,* (2012) also observed high membrane contributions for several test compounds including two of the current study (diazinon and diuron). Together these findings indicate that studies using methanol and water rinsing can result in highly variable POCIS sampling rates. It is recommended that a standardized protocol is developed for POCIS extraction and that the rinsing procedure applies water.

Interestingly, membrane uptake appears to be linear over the entire 28 days for many of the tested compounds. An alternative polyether sulfone (PES) membrane-only sampler may be a simple, quantitative solution for passive sampling of these and similar compounds, but the concept needs validation. Recently, Belles *et al.,* (2014) tested a nylon membrane POCIS-PHARM configuration, which appeared to be more suitable for hydrophobic compounds than the original PES sampler. The nylon sampler achieved higher *R*s and eliminated the lag phase for hydrophobic compounds, while the PES POCIS produced better results for the more hydrophilic compounds.

3.2 POCIS field calibrations

All water and POCIS pesticide detections for the site-specific field calibrations are presented in Appendices 10-13, with summaries for the two sites listed in Table 3.

The Folsom calibration resulted in varying pesticide detections depending on sampling time and technique (App. 10-11). Seven of twenty-three target pesticides (*i.e.*, 30%) were detected in composite water samples at some point and only two compounds, fipronil amide and fipronil sulfone, were detected with 100% success (n = 11). Although water detections were low, approximately fifty percent of the target pesticides were detected in POCIS. Together, nine pesticides were detected in POCIS after 28 days (carbaryl, fipronil, fipronil amide, fipronil sulfone, 2,4-D, MCPA, oryzalin, simazine and myclobutanil) whereas three compounds (imidacloprid, triclopyr and chlorothalonil) were randomly detected, indicating trace presence within the water. Additionally, six compounds (carbaryl, imidacloprid, 2,4-D, MCPA, simazine and myclobutanil) were not detected in water at any sampling time, however one compound (fipronil desulfinyl, 9% success in water) that was detected in water, was not detected in the POCIS.

Linear modeling of POCIS sampling rates is only valid if i) uptake in POCIS is linear throughout the deployment period and ii) the TWA water concentration can be determined. For this field experiment, compounds were accepted for modeling if water detection success exceeded 50% and coincided with detection in POCIS. For the Folsom calibration, fipronil, fipronil amide, and fipronil sulfone fulfilled these criteria. Fipronil and fipronil sulfone were present in water at very low levels and did not accumulate in POCIS in measurable amounts until day 14 (Fig. 4a). It was therefore not possible to derive *R*s for these compounds. Fipronil amide accumulated in POCIS in a linear fashion over the 28 day deployment (Fig. 4a). This compound was detected in POCIS below the reporting limit during the first 5 days of deployment indicating that the apparent lag phase is false. Linear regression derived a lag phase of 0.38 days and *R*s of 0.053 L/d (Table 2). This sampling rate is within the range, although lower, of that determined in the lab calibration (0.070 L/d; Table 2). These consistent findings support application of the derived sampling rates for fipronil amide at Folsom 1 and similar sites.

Field calibration of the POCIS in Salinas also displayed variable water detections between sampling days (App. 12-13), but detection success was generally higher while detected pesticides differed from those at Folsom (App. 10-11). In addition to the twenty-three POCIS target pesticides, four SPMD target compounds were detected with high frequency in both water and POCIS (dacthal, prometryn, propyzamide and tebuconazole). Thirteen compounds were randomly detected in water, however eight were detected 100% of the time. Furthermore, fifteen of the twenty-seven compounds were randomly detected in POCIS (App. 12). 2,4-D was consistently detected in POCIS, while four compounds (diazinon, dimethoate, malathion and prometon) were detected sporadically in POCIS; all five compounds were not detected in any water sample.

Nine compounds with potential for derivation of Salinas-specific sampling rates are plotted in Figures 4b-d. The field calibration of azoxystrobin, boscalid, and myclobutanil appears to be more successful than the laboratory calibration. All three had either a minor or no indication of a lag phase and exhibited linear uptake over the 28 day deployment (Fig. 4b). The minor lag

phases observed for azoxystrobin and boscalid can be explained by limited trace uptake (<RL) during the first 1-3 sampling days. The obtained sampling rates were 10-100 times higher than those determined in the laboratory calibration, and the sampling rate determined for azoxystrobin (0.231 L/d) compares well with those determined and reviewed in Ibrahim *et al.*, (2013). Also, for imidacloprid, field calibration resulted in an enhanced sampling rate (0.200 L/d *vs.*, 0.014, Table 2, Fig. 4c). This sampling rate is also relatively high compared to the laboratory calibration by Belles *et al.*, (2014), however is within the range of sampling rates common for POCIS, although varying flow rates should be considered. The water and POCIS detections were too low and fluctuated too much to determine sampling rates for methomyl and tebuconazole (Fig. 4c). Successful calibration was achieved for three unexpected compounds, dacthal, prometryn and propyzamide, which had been selected for uptake into the SPMDs due to their high log K_{ow}s (4.28, 3.51, 3.45, respectively; Fig. 4d). Dacthal uptake peaked after 17 days (Rs = 0.109), yet water concentration trends could only partially explain the observed peak, it is not clear if the observed non-linearity after D17 is general. Until further experiments are conducted, a maximum 17 day deployment will provide the most conservative quantitative assessment for dacthal. Prometryn and propyzamide exhibit log K_{ow}s near the range appropriate for POCIS and resulted in good sampling rates (0.254 and 0.208 L/d, respectively) that may be useful for quantification of TWA for these compounds at the Salinas site.

POCIS field calibration is challenging at sites of pulse and trace pesticide occurrences. Sporadic water detections prohibit robust determination of TWA water concentrations, which are prerequisites for derivation of a sampling rate. Field calibrations can be improved when spiking is possible (*e.g.*, Vermeirssen et al., 2011), however, spiking directly into waterways is obviously not ethically appropriate. In this study, we successfully calibrated one compound at Folsom 1 and seven compounds at the Salinas site. Unfortunately without overlap between the sites, it is not possible to compare sampling rates between them. The field sampling rates determined in this study are generally comparable with the rates determined in published laboratory calibration studies and support semi-quantitative use of POCIS for these compounds.

3.3 Site comparisons of pesticide detections in water and POCIS

The occurrence of polar pesticides fluctuated between site and time of year (Figures 5-6, Tables 3-5). POCIS target compounds were detected in higher abundance at Folsom during the summer compared to the spring and fall (Fig. 5), while higher abundance was observed in Salinas in the fall (Fig. 6). Detections at the Salinas site covered most of the POCIS compounds analyzed in this study, except for carbaryl, chlorothalonil, MCPA, fipronil amide and fipronil sulfide. At Folsom, 4 of 7 insecticides, 5 of 7 herbicides and 2 of 4 fungicides were detected.

Pesticide detections in water grab and composite samples also varied among sampling times within the same site and time of year (Appendices 10-17). Only two pesticides were detected with 100% frequency in water samples for every deployment event at the same site. Both boscalid and myclobutanil were consistently detected in water and POCIS (Fig. 6), whereas azoxystrobin was frequently detected at the Salinas. Of these three fungicides, only myclobutanil was detected in Folsom during the summer deployment (water and POCIS) and fall deployment (water only; Fig. 5). Chlorothalonil and its hydrolysis product were rarely detected at either site, however, it should be noted that analytical challenges may have obscured chlorothalonil data.

Fipronil and its products were well represented at the Folsom site during 2013 (Fig. 5). Fipronil sulfide was only detected in POCIS during the spring deployment, whereas the other fipronils were detected in both water (frequency varied) and POCIS. During the summer deployment, two fipronil amide and sulfone were detected 100% of the time (n=11) with an overall detection frequency of 80% for the deployments in 2013. Fipronil itself was detected at the highest frequency (80%) in the spring deployment. Fipronil desulfinyl was captured in water by chance during the summer deployment and only in POCIS during the fall deployment. In Salinas, fipronil and its degradates were less commonly detected (Fig. 6).

Imidacloprid was detected in water and POCIS in every deployment of the 2013 conducted in Salinas, while it was only detected randomly in Folsom in the spring and fall deployments. A water grab sample did capture a pulse of imidacloprid in Folsom during the fall deployment however it was not recovered in the POCIS. Of the remaining 'POCIS insecticides', diazinon, dimethoate and methomyl were not detected in Folsom at any time, but diazinon was detected in POCIS deployed in Salinas during the summer. Dimethoate was detected in Salinas in both water and POCIS in the fall, and methomyl was detected with 100% frequency in Salinas water grab samples during the summer deployment. Of all six deployments, both carbaryl (water grab sample; summer) and malathion (water grab sample; fall) were only detected once in Folsom. In Salinas results for malathion was detected in POCIS in both the spring and summer deployments, yet only detected in one water sample in the spring and fall deployments.

Detections of the herbicides 2,4-D, MCPA, oryzalin, simazine and triclopyr peaked in Folsom during the summer deployment. 2,4-D and triclopyr were detected at Folsom during each deployment although detection frequency varied. All herbicides, except MCPA, were detected at the Salinas site with highest abundance and water detection frequencies in the fall deployment. Diuron was also detected with high frequency in Salinas during the spring.

The relative success of POCIS *vs.* grab sampling varied. 2,4-D was detected in POCIS in all six deployments, but not once across the 42 water samplings. For 2,4-D, POCIS is clearly the most useful sampling technique. Diazinon, fipronil sulfide and OH-chlorothalonil were only detected once each in POCIS. In few cases, water detection frequency was surprisingly high without detection in POCIS (*e.g.*, fipronil sulfone during fall at Folsom; Fig. 5, and oryzalin in Salinas during fall; Fig. 6). For majority of the pesticides, however, water detection frequency was below 100% during most deployments. Overall, grab sampling only has merit to be successful if water detection frequency is 100%. When water detection is sporadic, POCIS is the better tool with higher chance of detection. Due to the low sampling rates (*i.e.*, volumes) achieved by POCIS, short pulses of pesticides at trace concentrations may still go unseen. In the intensive sampling scenarios undertaken during this research, grab samples captured pulses that were not detected in POCIS (Fig. 5 and 6). Most regulatory monitoring does not have the means to conduct such intensive screening, thus POCIS may be the most economical and integrative solution for screening of a number of pesticides, although it is not quantitative for all.

Overall, the Salinas site covered a broader spectrum of POCIS target pesticides compared to Folsom. The broader pesticide usage in Salinas was expected because this site is located in very close proximity to both agriculture and urban development, whereas the Folsom site only receives urban runoff. The results of the multiple deployments are a good indication of pesticides

used in urban and agricultural settings throughout a year. Although this study only targeted a suite of pesticides, it does not imply that these are the only pesticides occurring at these sites. Further studies are necessary to screen all possible pesticides used near these field sites.

3.4 Site comparisons of pesticide detections in water and SPMD

Hydrophobic pesticide occurrences were highly variable dependent on the site and time of year deployments occurred (Appendices 14-17; Figures 7-8; Tables 3-5).

The spring deployment detected the highest abundance of pesticides in Folsom. Detections included the insecticide chlorpyrifos (sampler only), in addition to the herbicides dacthal and pendimethalin; these herbicides were only detected in the spring deployment. Pendimethalin, was measured in 80% of collected water samples and detected in both POCIS and SPMD samplers, however dacthal was only measured in the sampler. Additional sampler only detections included cyhalothrin, cypermethrin and permethrin. The synergist PBO however, was measured in 40% on the water samples and in both POCIS and SMPDs during the spring deployment. Fall deployment resulted in detections of bifenthrin and permethrin in SPMDs but not in water. Data for these detections are presented in Tables 3-4.

During the summer deployment in Folsom, fipronil sulfone was captured in 100% of the water samples, however only fipronil sulfide was measured in the SPMDs. A few apparent pulses of tebuconazole were captured at Folsom by water grab, but not by SPMDs. Since tebuconazole was detected by POCIS, the polar sampler may be the better choice for this compound. Three compounds were detected in the summer at Folsom (bifenthrin, *cis*-permethrin and fipronil sulfide) although in the spring cypermethrin and PBO were measured in higher concentration at Folsom; bifenthrin was not detected in any samples collected during the spring deployment.

SPMD screenings in Salinas, during the spring, resulted in detection of the same compounds as in Folsom, in addition to one pyrethroid (fenpropathrin), several herbicides (oxyfluorfen, propyzamide and trifluralin) and one fungicide (pyraclostrobin); pendimethalin, was not detected in the sampler (Fig. 8). Results from the fall deployment did not result in as many pesticide detections as the spring. Prometryn was detected with 100% success rate in water samples during the summer and fall deployments despite going undetected in SPMDs. Also, summer results showed pendimethalin, pyraclostrobin and tebuconazole detections by water grab sampling on a few occasions without corresponding detection in SPMDs (Tables 3 and 5).

Spring deployed sampler concentrations were higher than those deployed in the summer and fall, for all but two pesticides (bifenthrin and fipronil sulfide) which were detected in SPMDs at both sites (Figures 7 and 8). Fall sampler concentrations were typically higher than those measured in summer. Interestingly, these results are similar to those observed for the POCIS compounds. The changes in detections between the three deployments, for hydrophobic compounds, may indicate a variation in pesticide use throughout the year by homeowners and those applied to agricultural fields. Further studies are necessary to determine if the measured concentrations reflect release of sediment-bound pesticides or current pesticide use. Alternatively, observations may be explained by high degradation and evaporative losses during the part of the year with higher temperatures and longer periods of sunlight. Again, it should be considered that flow and other environmental variations may be affecting the pesticide detections and ultimately the sampling rates.

Most hydrophobic compounds were present in water below the detection limit of a water grab sample. Particularly for the pyrethroid insecticides, the ability to detect the bioavailable fraction is important for risk assessment purposes. Few published studies have applied the SPMD for screening of pyrethroid insecticides. Unfortunately, this sampler lacks a PRC representative of pyrethroid compounds in order to be quantitative. We tested the loss of ^{13}C-*cis*-permethrin spiked into the samplers prior to deployment, however this compound did not partition back over the membrane into the water solution during deployment and therefore is not suitable as a PRC. The fact that the labeled pyrethroid compound is not lost from the sampler during deployment indicates that pyrethroids accumulate irreversibly in the SPMD and that the PRC concept is inappropriate for field-correction of pyrethroid sampling rates. Perhaps an alternative approach such as the co-deployment of dental plaster as a surrogate tool to correct for flow variation may be useful for this sampler as found by O'Brien *et al.*, (2012). Nevertheless, the consistent detection of hydrophobic pyrethroid insecticides and other pesticides in the SPMD support the application of this sampler over traditional grab sampling for screening of hydrophobic compounds.

4.0 Conclusions

Laboratory and field experiments were conducted to assess the applicability of POCIS and SPMD passive samplers as pesticide monitoring tools; these calibrations are necessary for a quantitative application of POCIS. Lab calibrations were conducted under static conditions to mimic static field conditions and represent a "slowest uptake" scenario, when diffusion across the membrane is expected to be slow. This experiment identified uptake lag phases for many of the POCIS compounds, which in turn prohibited the linear modeling needed to derive POCIS sampling rates for these pesticides. The static calibration experiment only provided minimal sampling rate data that should be interpreted with caution as the results were highly variable. Although the lack of sampling rates is unfortunate, the data does bring attention to the potential of other pesticides to behave in a similar manner if site specific flow conditions were to be near static conditions. To better understand lag phases and to gather a greater range of sampling rates, additional calibration experiments should be conducted under various flow conditions. The data collected here, under static conditions, should be considered qualitative. Extraction and analysis of POCIS membranes demonstrated that many of the tested compounds accumulate in membranes where they are retained and restricted from uptake in the POCIS sorbent. This finding is important because standardized POCIS extraction methods do not exist. Some laboratories use water, while others use methanol to rinse sorbent off membranes, thus increasing the likelihood of extracting pesticides from the membranes. These methodological discrepancies may lead to discrepancies in POCIS sampling rates determined by other labs and caution must be taken when comparing sampling rates between them.

Field calibration is very challenging for contaminants that are only present in pulses or in trace concentrations. Seven pesticide compounds (azoxystrobin, boscalid, dacthal, imidacloprid, myclobutanil, prometryn and propyzamide) were successfully calibrated for a northern California reclamation ditch receiving a mixture of urban and agricultural runoff, and one pesticide was calibrated for an urban site (fipronil amide). For several compounds, the field-derived sampling rates compared well with laboratory-derived published values. These findings

hold promise for POCIS as a more quantitative screening tool although for majority of the compounds tested here this sampler remains more suitable for qualitative purposes.
SPMD sampling rates can be field-corrected for compounds with appropriate PRCs. This study trialed SPMDs pre-injected with ^{13}C-labeled *cis*-permethrin to test its applicability as a PRC for pyrethroid insecticides. The labeled compound was fully recovered after all 28-day deployments, thus indicating that pyrethroid compounds accumulate into the sampler's triolein medium more irreversibly than other compounds (*e.g.,* PAHs and PCBs). Based on these findings, SPMDs containing a triolein medium are recommended as qualitative tools for pyrethroid insecticides. Alternative PRCs and/or other sampler types may better represent pesticides; further pesticide-specific research is necessary.

Multiple co-deployments of passive samplers in waters receiving urban and agricultural runoff allowed detection of a broad suite of pesticides, many of which went undetected by intensive grab and continuous water sampling. The field efforts revealed seasonal and site-specific variations in pesticide occurrences, demonstrating that the occurrence of many relevant pesticides is grossly underestimated through the occasional grab sampling commonly utilized by regulatory authorities. In few cases, small pulses were observed via grab sampling but were not captured in the samplers due to low sampling rates.

Additional studies are needed to comprehensively characterize the effects of environmental parameters such as flow conditions on pesticide sampling rates. Due to the extensive calibration efforts required, passive samplers may be best suited for qualitative screening purposes, particularly if the screening covers multiple sites. The pesticides calibrated here may be semi-quantitatively monitored for, in the future, for the specific sites selected in this study. Passive samplers enable simultaneous water monitoring at more sites and for a greater part of the calendar year than is most often possible due to budgetary constraints thus, prolonged deployment enables capture of episodic events that may be missed by traditional sampling regimes. Overall, this study supports the combined use of POCIS and SPMDs as a useful screening tool for field monitoring of pesticides used in California; future use is encouraged.

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Tables and Figures.

Table 1. Table of pesticide standards and chemical specific information. *Color codes: Green (log K_{ow} <1, POCIS), blue (log K_{ow} 2-3, POCIS), orange (log K_{ow}>3, POCIS), tan (log K_{ow}>3, SPMD) and red (log K_{ow}>3, both samplers).*

Target Chemical	CAS #	log K_{OW}[1,2,3]	Solubility	Pesticide Class	Sampler	Instrumental Analysis	RL
Methomyl	16752-77-5	0.6	58,000	Carbamate	POCIS	LC	10
Imidacloprid	138261-41-3	0.57	610	Neonicotinoid	POCIS	LC	10
Dimethoate	60-51-5	0.78	23,300	Organophosphate	POCIS	LC	10
Carbaryl	63-25-2	2.36	100	Carbamate	POCIS	LC	10
Malathion	121-75-5	2.36	143	Organophosphate	POCIS	LC	10
2,4-D	94-75-7	2.81	677	Phenoxy	POCIS	LC	10
Diuron	330-54-1	2.68	42	Phenyl urea	POCIS	LC	10
Boscalid	188425-85-6	2.96	4.6	Pyridine	POCIS	LC	10
Triclopyr	55335-06-3	2.53	440	Pyridine	POCIS	LC	10
Azoxystrobin	131860-33-8	2.5	6	Strobilurin	POCIS	LC	10
Prometon	1610-18-0	2.99	750	Triazine	POCIS	LC	10
Simazine	122-34-9	2.18	6.2	Triazine	POCIS	LC	10
Myclobutanil	88671-89-0	2.89	132	Triazole	POCIS	LC	10
Oryzalin	19044-88-3	3.73	2.5	Aniline	POCIS	LC	10
MCPA	94-74-6	3.25	630	Phenoxy	POCIS	LC	10
OH-chlorothalonil	28343-61-5	3.09	116	Product	POCIS	LC	10
Chlorothalonil	1897-45-6	3.05	0.81	Chloronitrile	POCIS	GC	6
Fipronil	120068-37-3	4	1.9	Phenylpyrazole	POCIS	GC	6
Fipronil amide	205650-69-7	N/A	N/A	Product	POCIS	GC	6
Fipronil desulfinyl	205650-65-3	4.63	0.4	Product	POCIS	GC	6
Fipronil sulfide	120067-83-6	4.77	0.2	Product	POCIS	GC	6
Fipronil sulfone	120068-36-2	3.68	1	Product	POCIS	GC	6
Propyzamide	23950-58-5	3.43	15	Amide	SPMD	GC	6
Pendimethalin	40487-42-1	5.2	0.33	Aniline	SPMD	GC	6
Trifluralin	1582-09-8	5.34	0.184	Aniline	SPMD	GC	6
Metolachlor	51218-45-2	3.13	530	Chloroacetanilide	SPMD	GC	6
Oxyfluorfen	42874-03-3	4.73	0.116	Nitrophenyl ether	SPMD	GC	6
Chlorpyrifos	2921-88-2	4.96	1.12	Organophosphate	SPMD	GC	6
Dacthal	1861-32-1	4.28	0.5	Phthatalic acid	SPMD	GC	6
Bifenthrin	82657-04-3	6	0.001	Pyrethroid	SPMD	GC	6
Cyfluthrin	68359-37-5	5.95	0.003	Pyrethroid	SPMD	GC	6
Cyhalothrin	68085-85-8	6.9	0.005	Pyrethroid	SPMD	GC	6
Cypermethrin	52315-07-8	6.6	0.004	Pyrethroid	SPMD	GC	6
Deltamethrin	52918-63-5	6.2	0.002	Pyrethroid	SPMD	GC	6
Esfenvalerate	66230-04-4	6.22	0.002	Pyrethroid	SPMD	GC	6
Fenpropathrin	39515-41-8	5.7	0.33	Pyrethroid	SPMD	GC	6
Permethrin	52645-53-1	6.5	0.006	Pyrethroid	SPMD	GC	6
Pyraclostrobin	175013-18-0	3.99	1.9	Strobilurin	SPMD	GC	6
Prometryn	7287-19-6	3.51	33	Triazine	SPMD	GC	6
Tebuconazole	107534-96-3	3.7	36	Triazole	SPMD	GC	6
PBO*	51-03-6	4.75	14.3	Synergist*	SPMD	GC	6
Diazinon	333-41-5	3.81	40	Organophosphate	Both	GC	6

*CAS = chemical abstract service number; K_{OW} = octanol-water partition coefficient; RL = reporting limit (ng/sample), where sample may be a sampler or 1 L of water. RL is the instrument detection limit or the calibration limit whichever is highest. For some GC compounds the RL varied. RL higher than 6 ng/sample are reported in the data tables. GC = gas chromatography; LC = liquid chromatography. *PBO = piperonyl butoxide, a synergist added to pyrethroid and other pesticide formulations.*

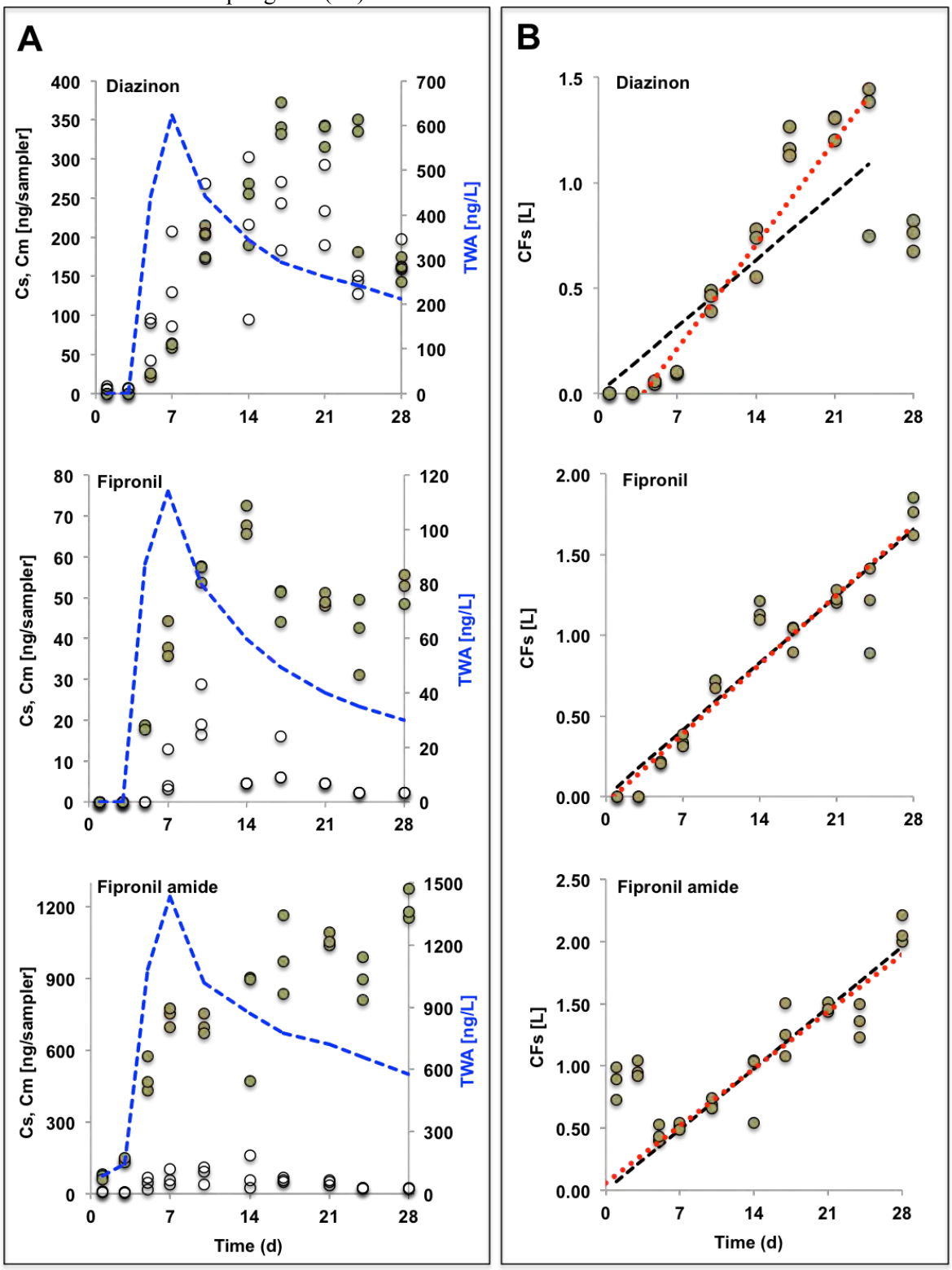
[1.] Values are from the SRC online database, [2.] Fipronil degradation products data from Walse et al., 2004, [3.] Data for boscalid, myclobutanil, pendimethalin, pyraclostrobin and tebuconazole from PPDB online database.

Table 2. POCIS sampling rates and lag phases determined in the calibration experiments.
Color-codes: Green (log K_{ow} <1), blue (log K_{ow} 2-3) and tan (log K_{ow}>3).

Target pesticide	Lab calibration				Field calibration			
	***R*s (L/d)**	**Peak day**	***R*s$_{tot}$ (L/d)**	**Lag phase (d)**	***R*s (L/d)**	**Lag phase (d)**	**Peak day**	**Site**
Dimethoate	N/A	Steady state	N/A	7				
Imidacloprid	0.014	17	0.031	None (burst)	0.200	None (burst)	28	S
Methomyl	N/A	Steady state	N/A	None				
2,4-D	N/A	21	N/A	None (burst)				
Azoxystrobin	0.0030	17	0.044	5.3	0.231	1.3	28	S
Boscalid	0.0048	17	0.036	5.2	0.051	None	28	S
Carbaryl	0.0014	21	0.019	7.4				
Diuron	0.003	17	0.062	7.6				
Malathion	N/A	24	N/A	17				
Myclobutanil	0.01	21	0.026	None	0.121	None	28	S
Prometon	0.0083	17	0.014	None (burst)				
Simazine	0.0049	17	0.025	0.3				
Triclopyr	0.035*	24	0.053*	4.8				
Chlorothalonil	N/A	N/A	0.0042	N/A				
OH-chlorothalonil	0.23*	21	0.083*	7.5				
Dacthal					0.109	1-3	17	S
Diazinon	0.054	24	0.087	4				
Fipronil	0.059	28	0.065	0.7				
Fipronil amide	0.070	28	0.073	None (-0.9)	0.053	0.38	28	F
Fipronil desulfinyl	0.038	28	0.051	2.4				
Fipronil sulfide	0.031	28	0.046	3.7				
Fipronil sulfone	0.026	28	0.058	3.9				
MCPA	0.082*	21	0.040*	None (burst)				
Oryzalin	0.005	21	0.083	8.1				
Prometryn					0.254	None	28	S
Propyzamide					0.208	None	28	S

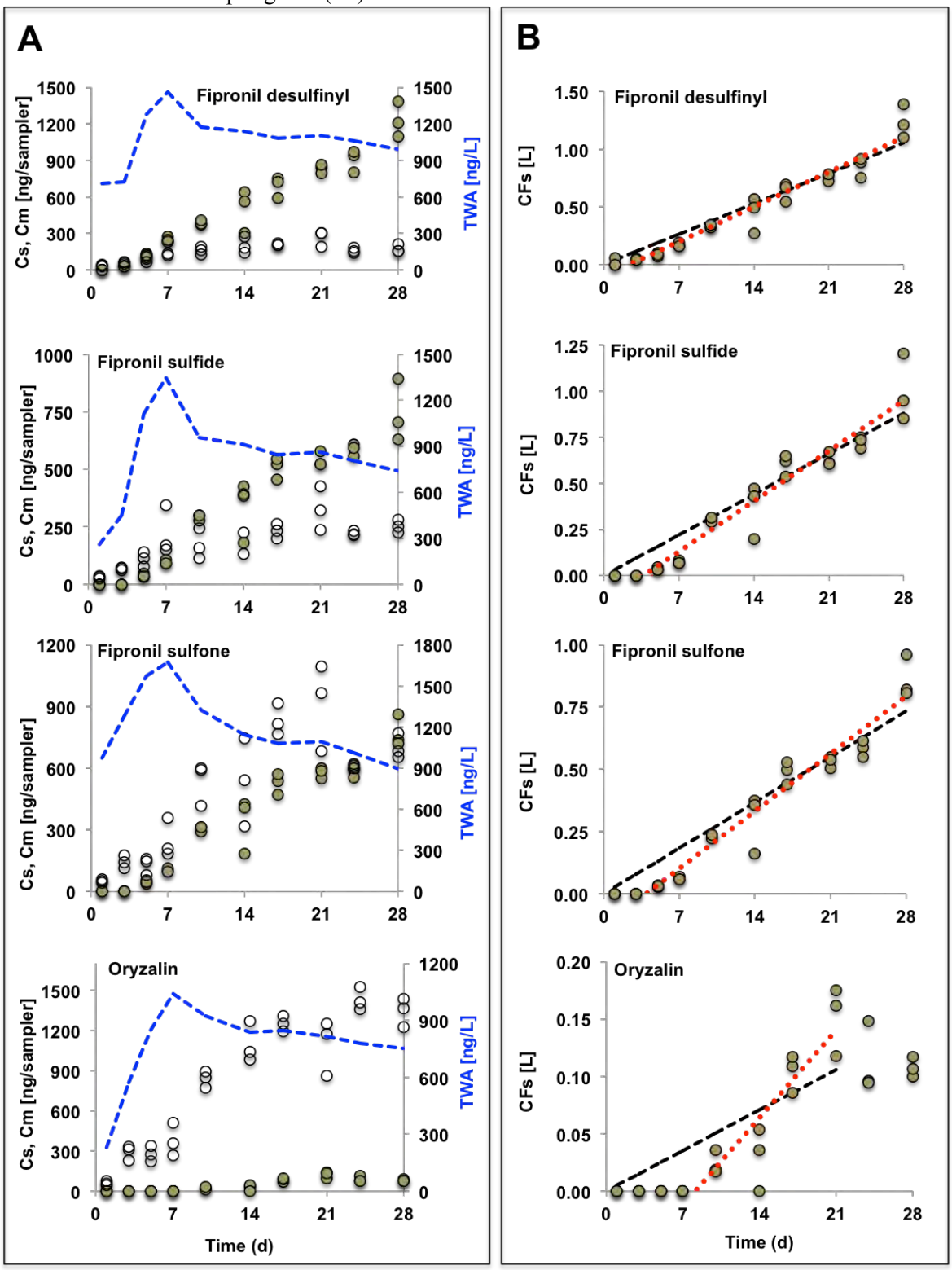
*Rs is the modeled sampling rate (sorbent-only, i.e., common method). Peak day indicates the day of peak uptake used to determine Rs. Rs_{tot} is the combined sorbent and membrane accumulation. The concentration factor (CF) approach was applied for compounds with fluctuating water concentrations: low-soluble compounds in the lab study (Fig. 1a-c) and for field-calibrations (Fig.4). *Manual calculation of Rs (when modeling was not possible. Values are tentative). N/A = not applicable. F = Folsom, S = Salinas.*

Figure 1a. Pesticide uptake kinetics in the POCIS laboratory calibration. **A**: Measured pesticide concentrations in water (TWA, time-weighted average; blue line), POCIS sorbent (Cs, sand circles) and membranes (Cm, clear circles) over the 28 d experiment. **B**: Sorbent concentration factors (CF_S) against time. Note: CFs/t = sampling rate (Rs).



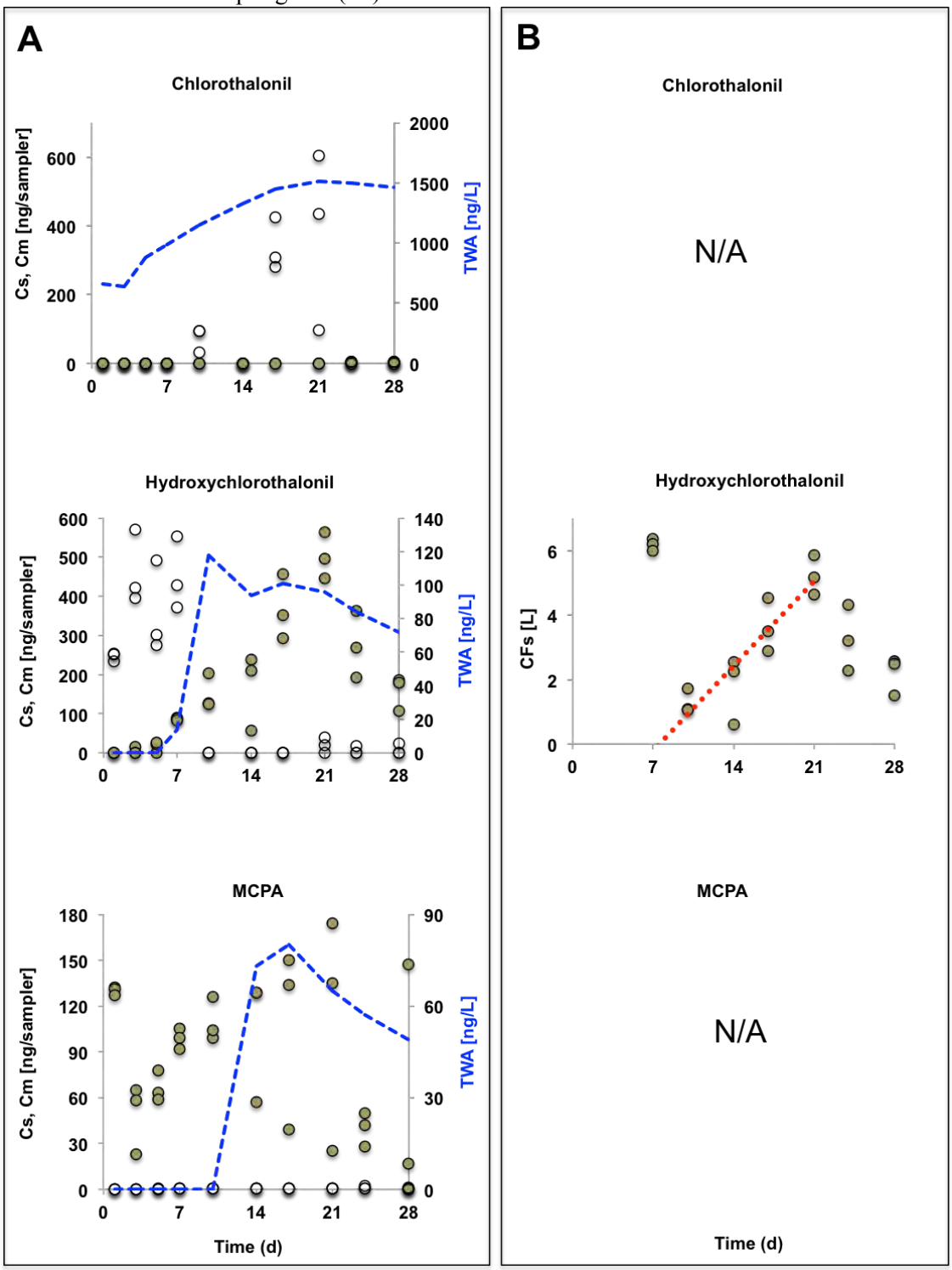
Black and red lines depict the linear regressions used to predict Rs and lag phases, respectively.

Figure 1b. Pesticide uptake kinetics in the POCIS laboratory calibration. **A**: Measured pesticide concentrations in water (TWA, time-weighted average; blue line), POCIS sorbent (Cs, sand circles) and membranes (Cm, clear circles) over the 28 d experiment. **B**: Sorbent concentration factors (CF_S) against time. Note: CFs/t = sampling rate (Rs).



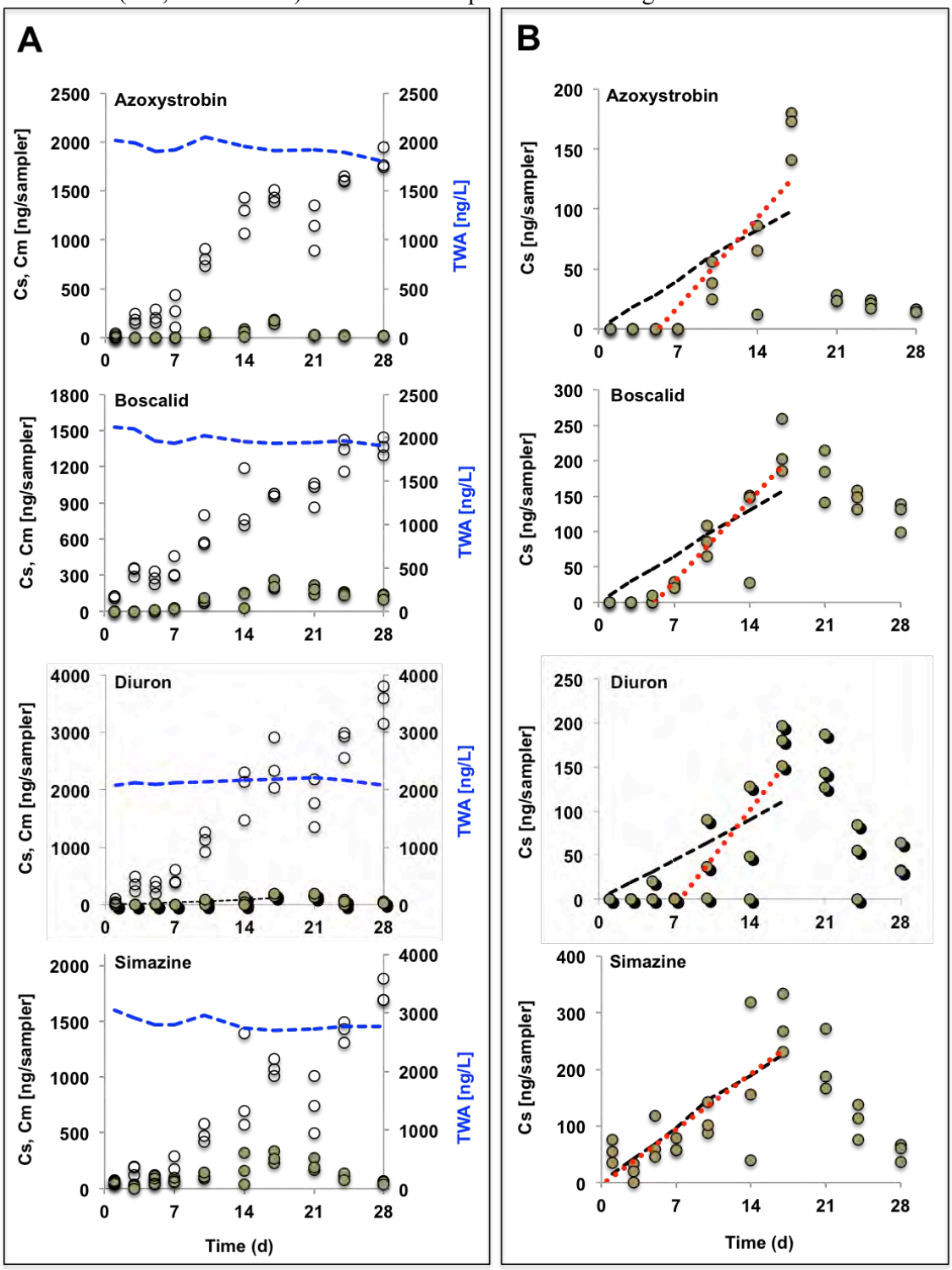
Black and red lines depict the linear regressions used to predict Rs and lag phases, respectively.

Figure 1c. Pesticide uptake kinetics in the POCIS laboratory calibration. **A**: Measured pesticide concentrations in water (TWA, time-weighted average; blue line), POCIS sorbent (Cs, sand circles) and membranes (Cm, clear circles) over the 28 d experiment. **B**: Sorbent concentration factors (CF_S) against time. Note: CFs/t = sampling rate (Rs).



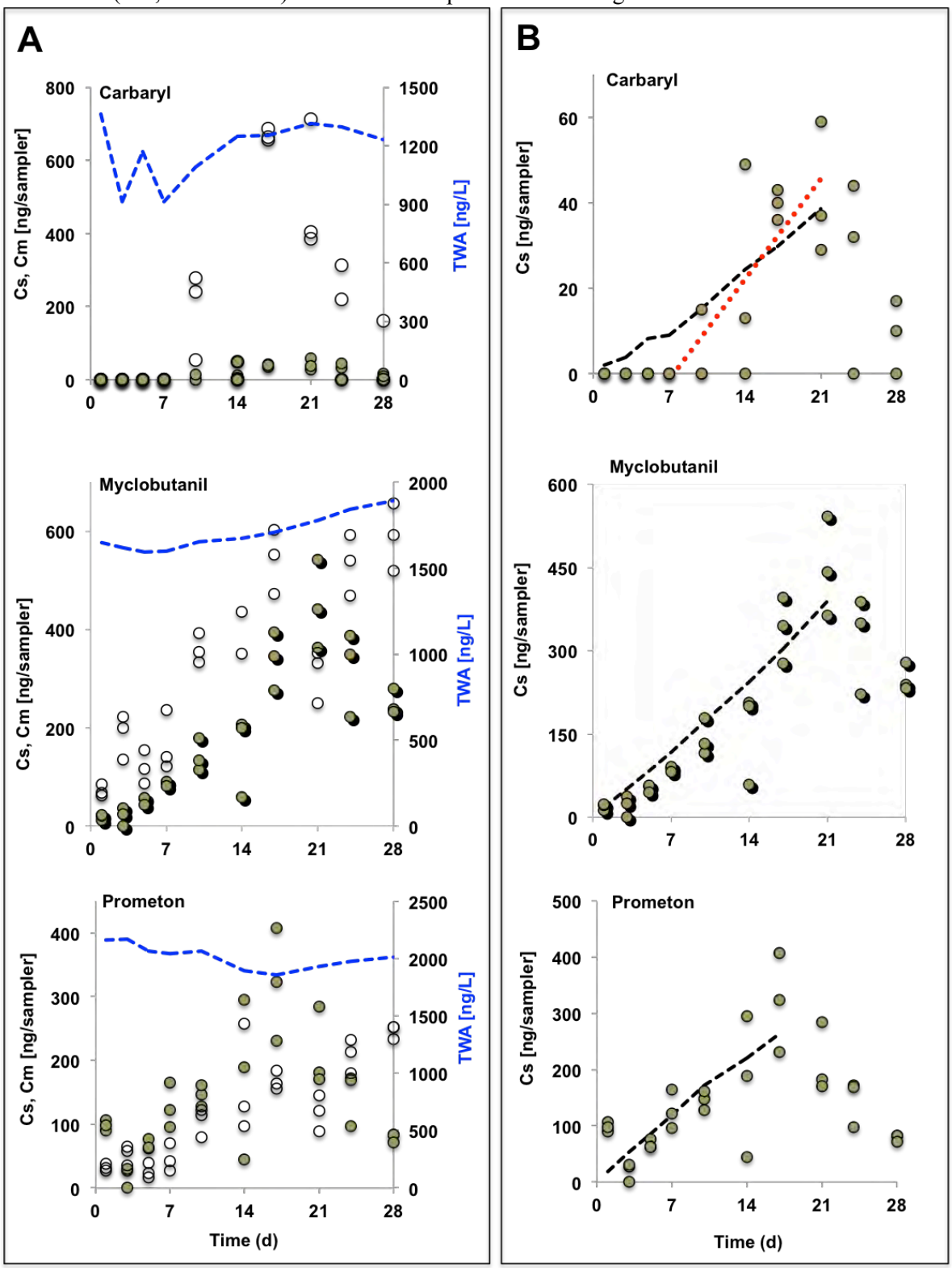
Red line depicts linear regression used to predict the lag phase for OH-chlorothalonil. CF could only be determined for OH-chlorothalonil from Day 7. CF could not be determined for chlorothalonil and MCPA. Linear regression did not enable determination of Rs.

Figure 2a. Pesticide uptake kinetics in the POCIS laboratory calibration. **A**. Measured pesticide concentrations in water (TWA, time-weighted average; blue line), POCIS sorbent (Cs, sand circles) and membranes (Cm, clear circles) over the 28 d experiment. **B**: Cs against time.



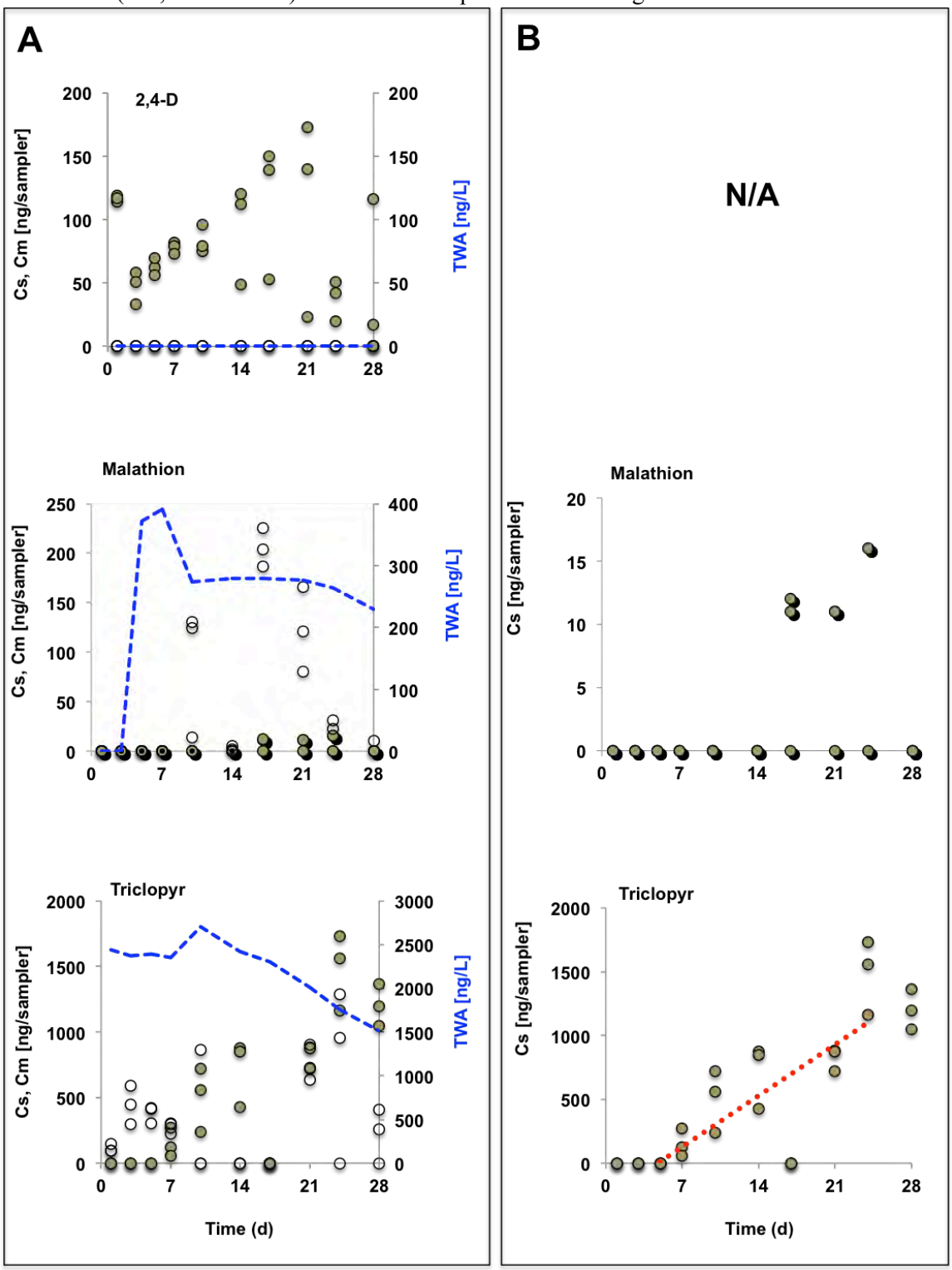
Black and red lines depict the linear regressions used to predict sampling rates and lag phases, respectively.

Figure 2b. Pesticide uptake kinetics in the POCIS laboratory calibration. **A.** Measured pesticide concentrations in water (TWA, time-weighted average; blue line), POCIS sorbent (Cs, sand circles) and membranes (Cm, clear circles) over the 28 d experiment. **B**: Cs against time.



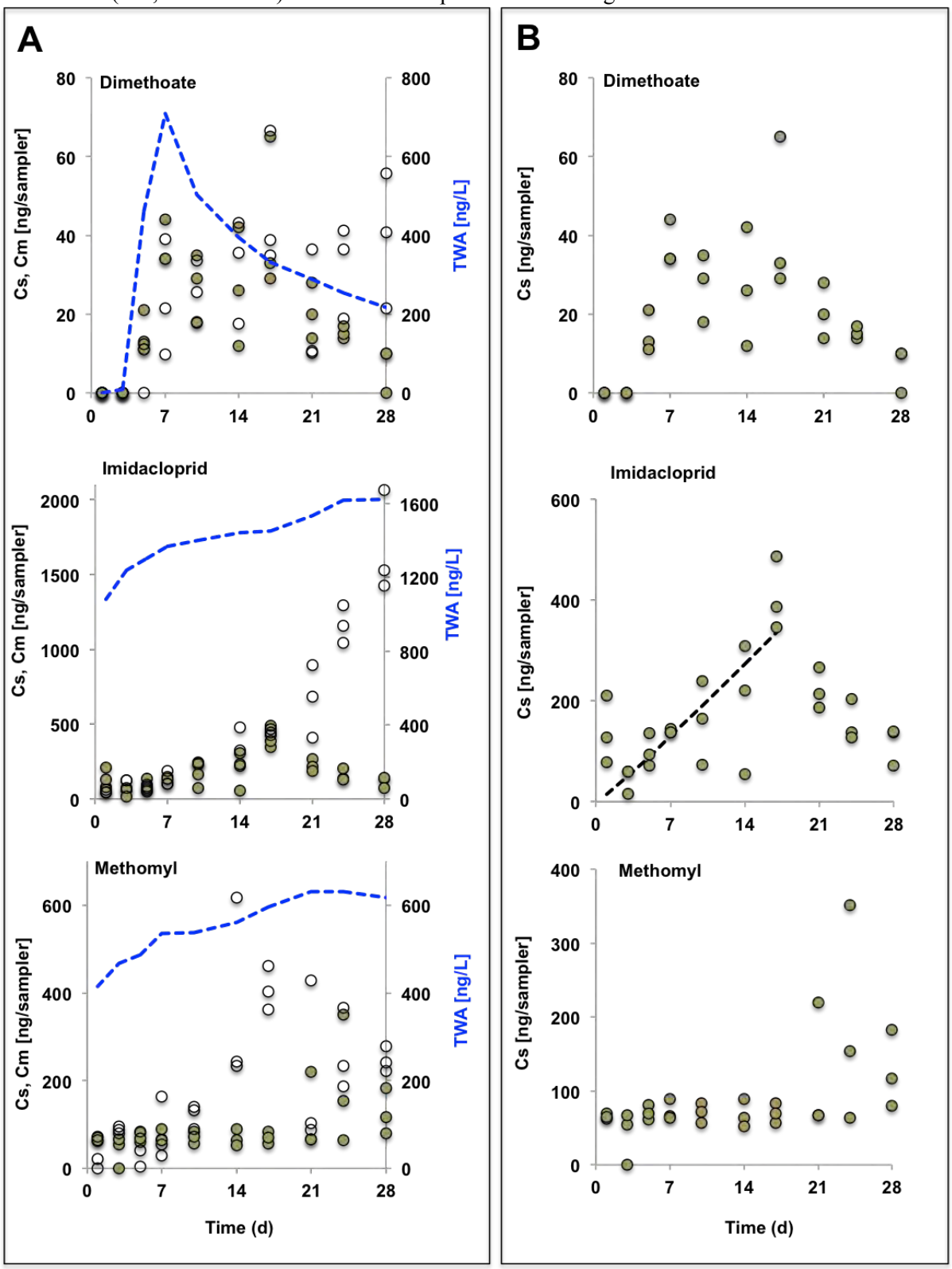
Black and red lines depict the linear regressions used to predict sampling rates and lag phases, respectively.

Figure 2c. Pesticide uptake kinetics in the POCIS laboratory calibration. **A:** Measured pesticide concentrations in water (TWA, time-weighted average; blue line), POCIS sorbent (Cs, sand circles) and membranes (Cm, clear circles) over the 28 d experiment. **B:** Cs against time.



The red line depicts the linear regression used to predict the lag phase for triclopyr.

Figure 3. Pesticide uptake kinetics in the POCIS laboratory calibration. **A:** Measured pesticide concentrations in water (TWA, time-weighted average; blue line), POCIS sorbent (Cs, sand circles) and membranes (Cm, clear circles) over the 28 d experiment. **B**: Cs against time.



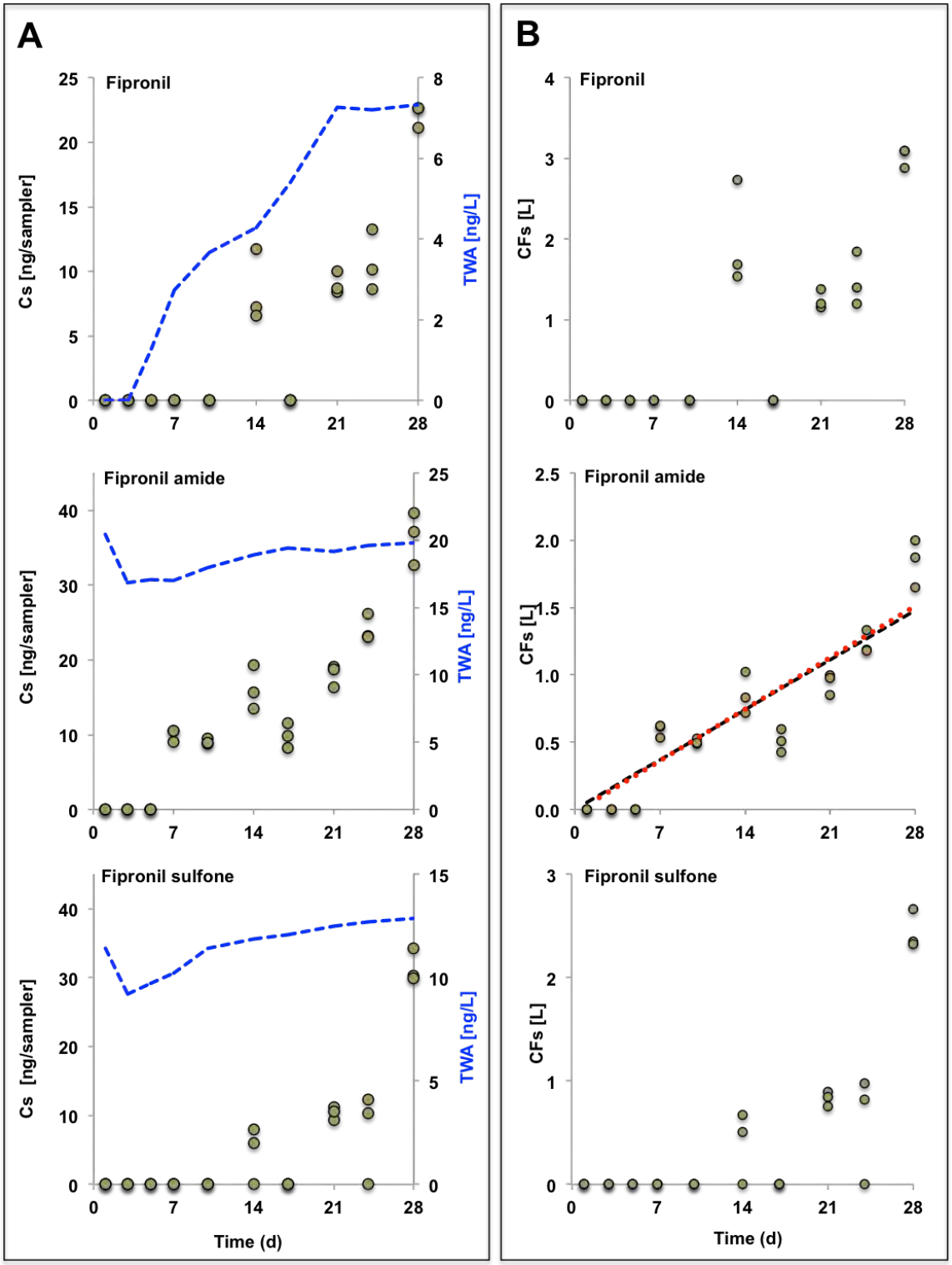
The black line depicts the linear regression used to predict the sampling rate for imidacloprid.

Table 3. Summary of pesticide detections in Folsom and Salinas during the summer calibration study (July and August 2013). *Color code: grey (POCIS compounds) and white (SPMD compounds).*

Target pesticide	Water freq. (%) (Folsom)	POCIS D28 (Folsom)	SPMD D28 (Folsom)	Water freq. (%) (Salinas)	POCIS D28 (Salinas)	SPMD D28 (Salinas)
2,4-D	0	+		0	+	
Azoxystrobin	0	ND		100	+	
Boscalid	0			100	+	
Carbaryl	0	+		0	ND	
Chlorothalonil	28	ND		0		
OH-chlorothalonil	0	ND		0	ND	
Diazinon	0	ND		0	+	ND
Dimethoate	0	ND		0	ND	
Diuron	0	ND		0	ND	
Fipronil	55	+		9	+	
Fipronil amide	100	+		0	ND	
Fipronil desulfinyl	9	ND		0	ND	
Fipronil sulfide	0	ND	+	0	ND	
Fipronil sulfone	100	+		0	ND	
Imidacloprid	0	ND		100	+	
Malathion	0	ND		0	+	
MCPA	0	+		0	ND	
Methomyl	0	ND		100	ND	
Myclobutanil	0	+		100	+	
Oryzalin	18	+		18	ND	
Prometon	0	ND		0	+	
Simazine	0	+		27	+	
Triclopyr	9	ND		18	ND	
Bifenthrin	0		+	0		+
Chlorpyrifos	0		ND	0		+
Cyfluthrin	0		ND	0		ND
Cyhalothrin	0		ND	0		+
Cypermethrin	0		ND	0		+
Dacthal	0		ND	100	+	+
Deltamethrin	0		ND	0		ND
Esfenvalerate	0		ND	0		ND
Fenpropathrin	0		ND	0		ND
Metolachlor	0		ND	0	ND	ND
Oxyfluorfen	0		ND	100		+
PBO	0		ND	9		+
Pendimethalin	18		ND	0		ND
Permethrin	18		+	0		+
Prometryn	0		ND	100	+	ND
Propyzamide	0		ND	100	+	+
Pyraclostrobin	0		ND	73		+
Tebuconazole	9		ND	55	+	ND
Trifluralin	0		ND	0		ND

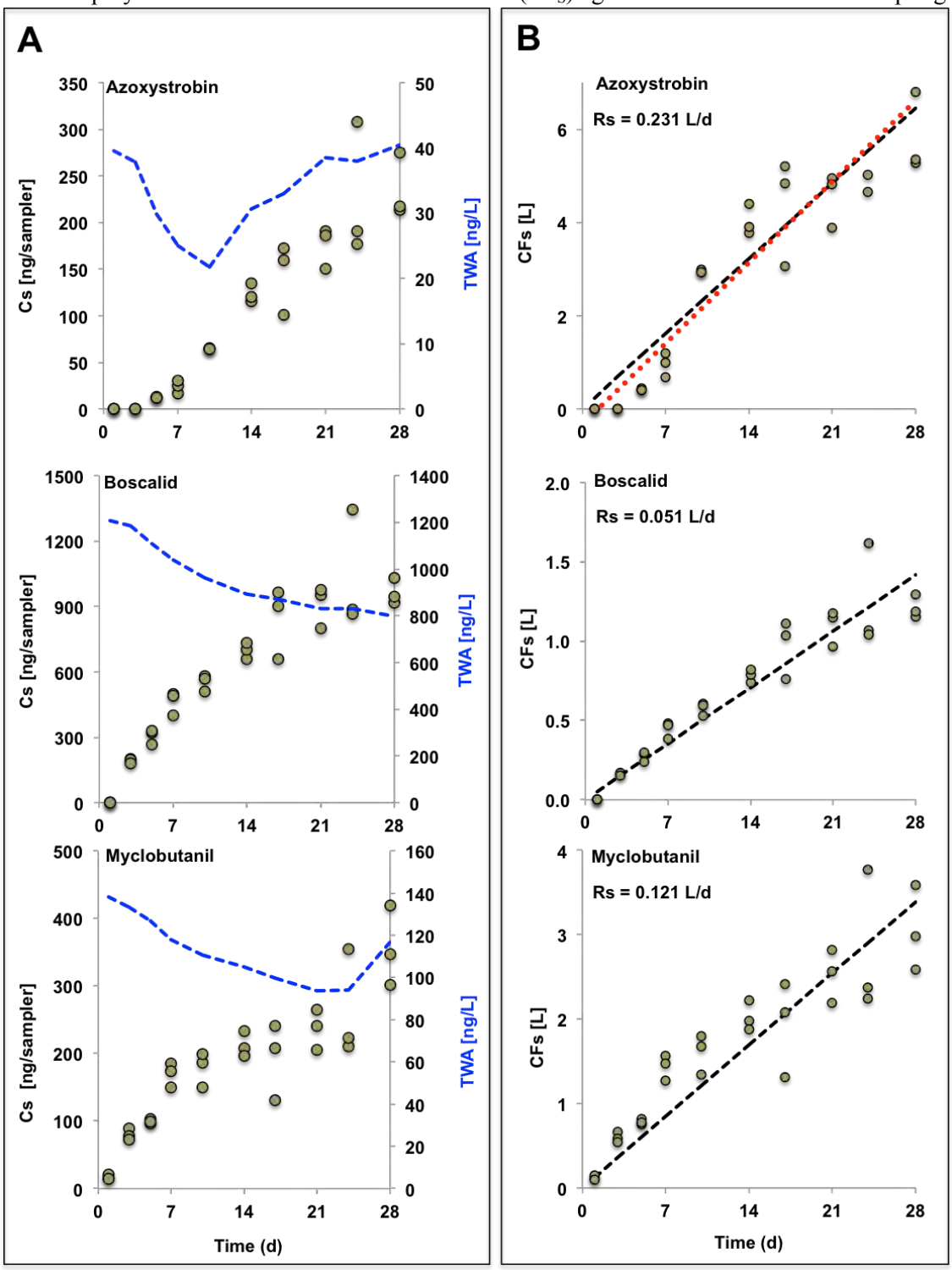
Water freq. refers to detection frequency of composite water samples collected throughout the sampler deployment (n=11). D# denotes day of sampling. Sampler detections are given for D28 (3 replicate samplers for each type). ND = non-detect (includes compounds <3x blank). + = detected above the reporting limit (Table 1) in all replicates. (All GC compounds were screened for in SPMDs). SPMD compounds are only noted in the POCIS columns if detected.

Figure 4a. Pesticide uptake kinetics in the POCIS field calibration in Folsom. **A:** Measured pesticide concentrations in water (TWA, time-weighted average) and POCIS sorbent (Cs, sand circles) over the 28 d field deployment. **B**: POCIS concentration factors (CF_S) against time. Note: CFs/t = sampling rate (Rs).



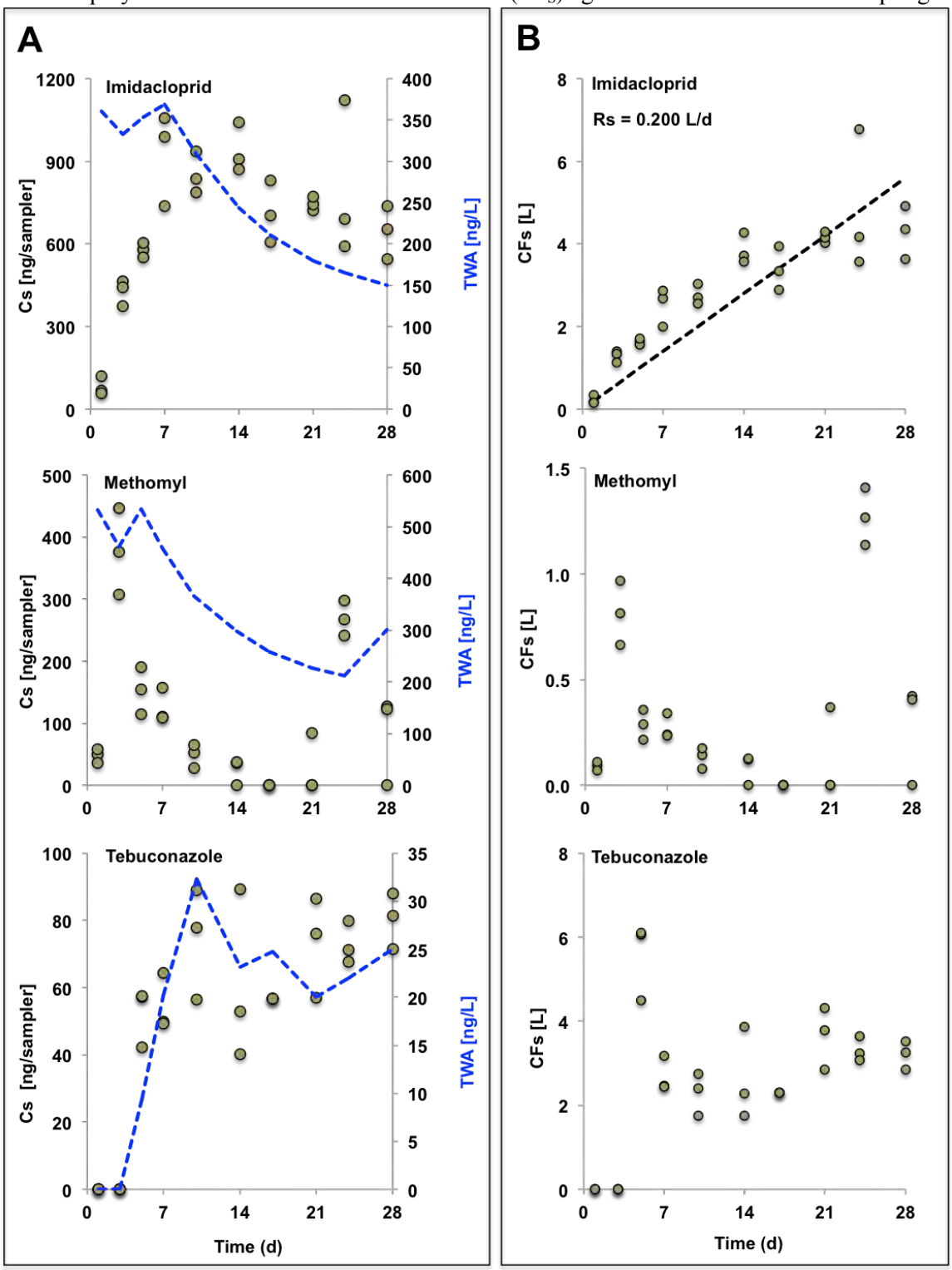
Black and red lines depict the linear regressions used to predict Rs and lag phases, respectively. Rs is the sampling rate.

Figure 4b. Pesticide uptake kinetics in the POCIS field calibration in Salinas. **A.** Measured pesticide concentrations in water (TWA, time-weighted average) and POCIS sorbent (Cs, sand circles) over the 28 d field deployment. **B**: POCIS concentration factors (CF_S) against time. Note: CFs/t = sampling rate (Rs).



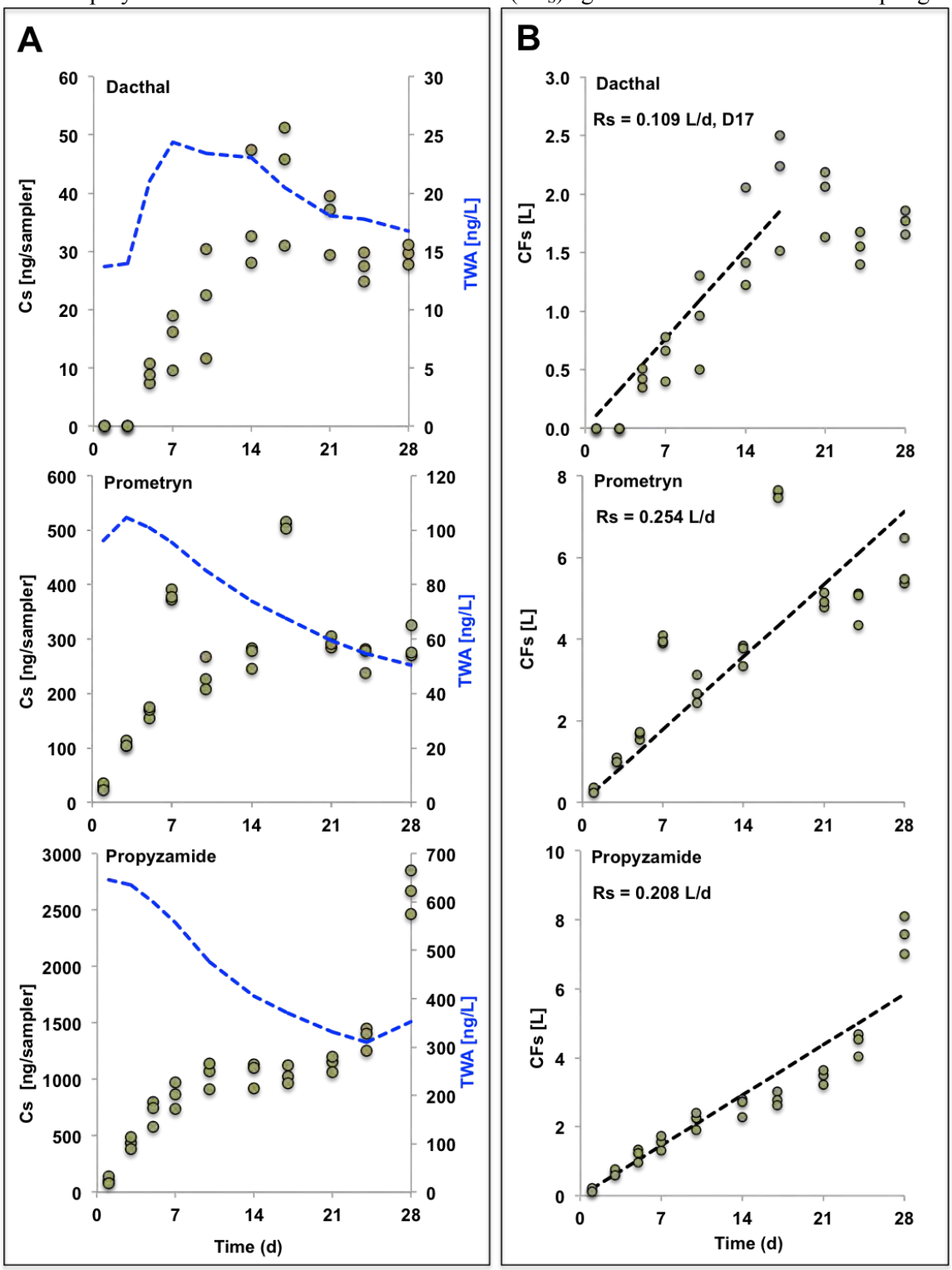
Black and red lines depict the linear regressions used to predict Rs and lag phases, respectively. Rs is the sampling rate.

Figure 4c. Pesticide uptake kinetics in the POCIS field calibration in Salinas. **A:** Measured pesticide concentrations in water (TWA, time-weighted average) and POCIS sorbent (Cs, sand circles) over the 28 d field deployment. **B**: POCIS concentration factors (CF_S) against time. Note: CFs/t = sampling rate (Rs).



Black and red lines depict the linear regressions used to predict Rs and lag phases, respectively. Rs is the sampling rate.

Figure 4d. Pesticide uptake kinetics in the POCIS field calibration in Salinas. **A:** Measured pesticide concentrations in water (TWA, time-weighted average) and POCIS sorbent (Cs, sand circles) over the 28 d field deployment. **B**: POCIS concentration factors (CF_S) against time. Note: CFs/t = sampling rate (Rs).



Black and red lines depict the linear regressions used to predict Rs and lag phases, respectively. Rs is the sampling rate

Table 4. Summary of pesticide detections in Folsom during the spring and fall deployments (Feb-Mar and October 2013). *Color code: grey (POCIS compounds) and white (SPMD compounds).*

Target pesticide	Water freq. (%) (Spring)	POCIS D28 (Spring)	SPMD D28 (ng/sampler) (Spring)	Water freq. (%) (Fall)	POCIS D28 (Fall)	SPMD D28 (Fall)
2,4-D	0	+		0	+	
Azoxystrobin	0	ND		0	ND	
Boscalid	0	ND		0	ND	
Carbaryl	0	ND		0	ND	
Chlorothalonil	20	ND		0	ND	
OH-chlorothalonil	0	ND		0	ND	
Diazinon	0	ND		0	ND	
Dimethoate	0	ND		0	ND	
Diuron	0	ND		0	ND	
Fipronil	80	+		20	+	
Fipronil amide	60	+		80	+	
Fipronil desulfinyl	60	+		0	+	
Fipronil sulfide	0	+		0	ND	
Fipronil sulfone	60	+		80	ND	
Imidacloprid	40	+		20	ND	
Malathion	0	ND		20	ND	
MCPA	0	ND		0	ND	
Methomyl	0	ND		0	ND	
Myclobutanil	0	ND		0	ND	
Oryzalin	0	ND		0	ND	
Prometon	0	ND		0	ND	
Simazine	40	+		0	ND	
Triclopyr	0	+		20	+	
Bifenthrin	0		ND	0		+
Chlorpyrifos	0		+	0		ND
Cyfluthrin	0		ND	0		ND
Cyhalothrin	0		+	0		ND
Cypermethrin	0		+	0		ND
Dacthal	0		+	0		ND
Deltamethrin	0		ND	0		ND
Esfenvalerate	0		ND	0		ND
Fenpropathrin	0		ND	0		ND
Metolachlor	0		ND	0		ND
Oxyfluorfen	0		ND	0		ND
PBO*	40	+	+	0		ND
Pendimethalin	80	+	+	0		ND
Permethrin	0		+	0		+
Prometryn	0		ND	0		ND
Propyzamide	0		ND	0		ND
Pyraclostrobin	0		ND	0		ND
Tebuconazole	40	+	ND	0	+	ND
Trifluralin	0		ND	0		ND

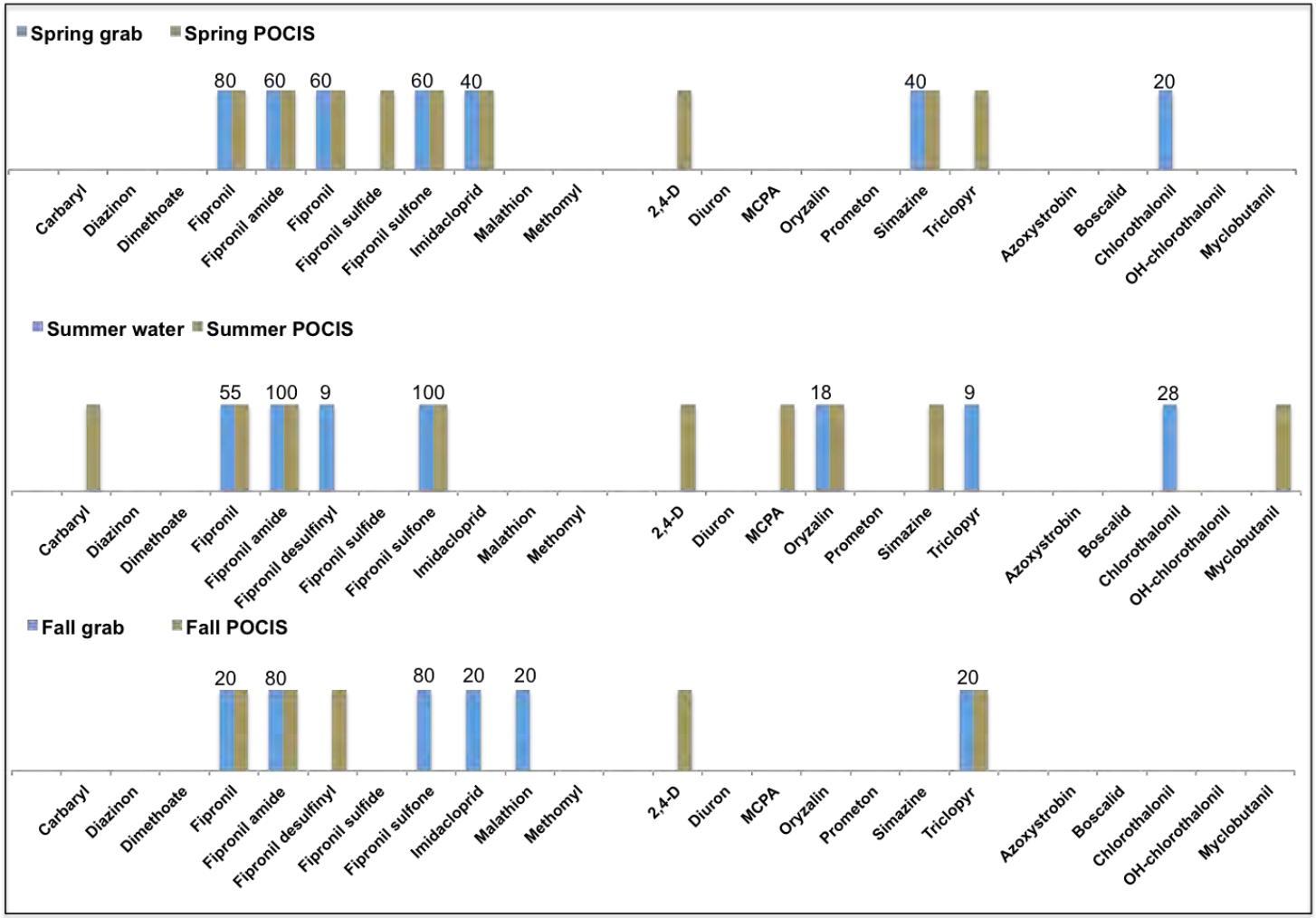
Water freq. refers to detection frequency of composite water samples collected throughout the sampler deployment (n=5). D# denotes day of sampling. Sampler detections are given for D28 (3 replicate samplers for each type). ND = non-detect (includes compounds <3x blank). + = detected above the reporting limit (Table 1) in all replicates. (All GC compounds were screened for in SPMDs). SPMD compounds are only noted in the POCIS column if detected.

Table 5. Summary of pesticide detections in Salinas during the spring and fall deployments (April and October 2013). *Color code: grey (POCIS compounds) and white (SPMD compounds).*

Target pesticide	Water freq. (%) (Spring)	POCIS D28 (Spring)	SPMD D28 (Spring)	Water freq. (%) (Fall)	POCIS D28 (Fall)	SPMD D28 (Fall)
2,4-D	0	+		0	+	
Azoxystrobin	80	+		100	+	
Boscalid	100	+		100	+	
Carbaryl	0	ND		0	ND	
Chlorothalonil	0	ND		0	ND	
OH-chlorothalonil	0	ND		0	+	
Diazinon	0	ND		0	ND	
Dimethoate	0	ND		80	+	
Diuron	80	+		100	+	
Fipronil	0	ND		60	+	
Fipronil amide	0	ND		0	ND	
Fipronil desulfinyl	0	+		60	+	
Fipronil sulfide	0	ND	+	0	ND	+
Fipronil sulfone	20	ND		20	ND	
Imidacloprid	60	+		100	+	
Malathion	20	+		20	ND	
MCPA	0	ND		0	ND	
Methomyl	0	ND		0	ND	
Myclobutanil	100	+		100	+	
Oryzalin	0	ND		60	ND	
Prometon	0	ND		40	ND	
Simazine	0	ND		60	+	
Triclopyr	0	ND		0	ND	
Bifenthrin	0		+	0		+
Chlorpyrifos	80		+	0		+
Cyfluthrin	0		+	0		ND
Cyhalothrin	0		+	0		+
Cypermethrin	0		+	0		ND
Dacthal	100	+	+	100	+	+
Deltamethrin	0		ND	0		ND
Esfenvalerate	0		ND	0		ND
Fenpropathrin	0		+	0		ND
Metolachlor	0	ND	ND	0		ND
Oxyfluorfen	100	+	+	80		+
PBO*	100		+	80		+
Pendimethalin	20		ND	40		ND
Permethrin	0		+	0		+
Prometryn	80	+	ND	100	+	ND
Propyzamide	100	+	+	80		+
Pyraclostrobin	100		+	40		ND
Tebuconazole	0		ND	0		ND
Trifluralin	20	+	+	0		ND

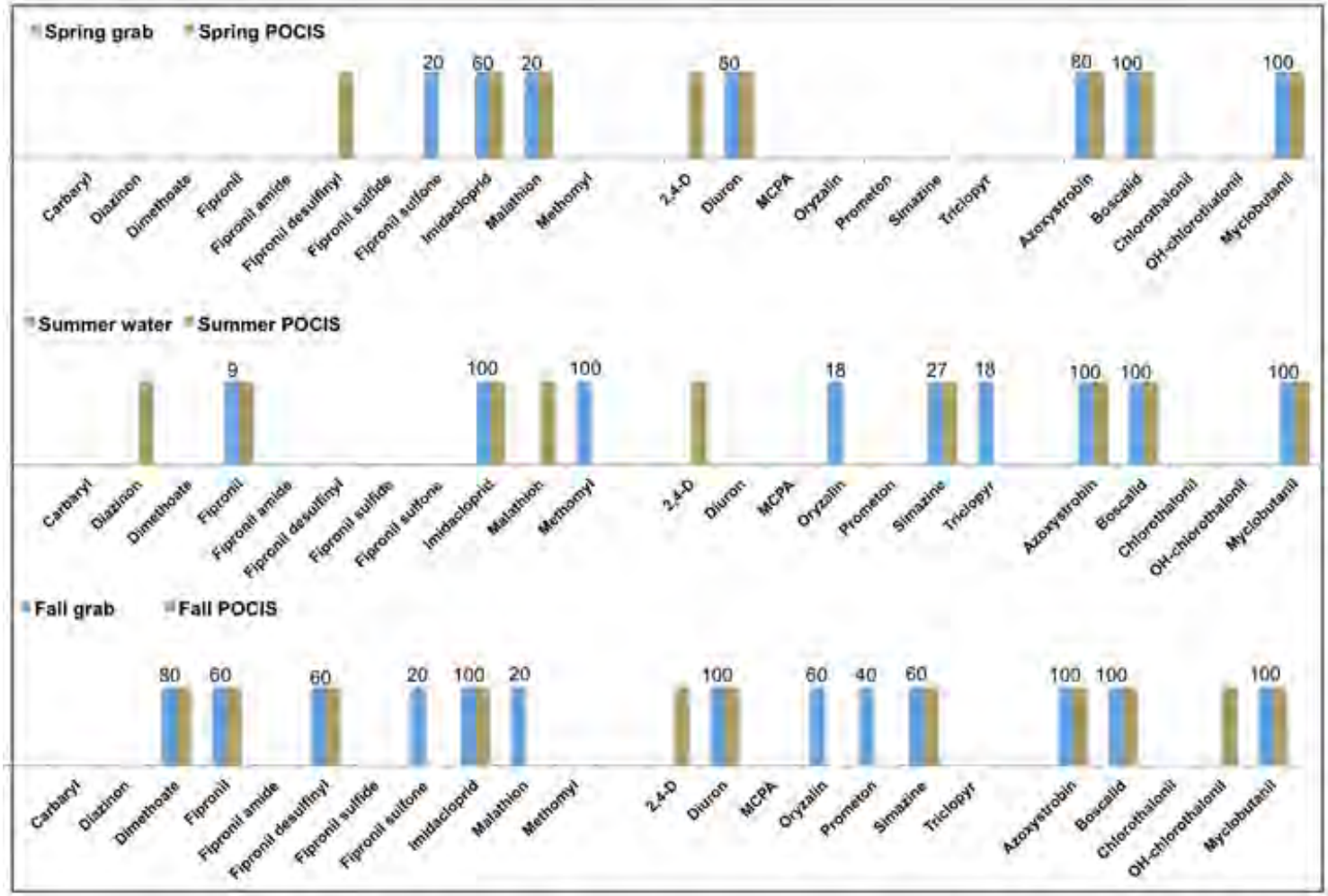
Water freq. refers to detection frequency of composite water samples collected throughout the sampler deployment (n=5). D# denotes day of sampling. Sampler detections are given for D28 (3 replicate samplers for each type). ND = non-detect (includes compounds <3x blank). + = detected above the reporting limit (Table 1) in all replicates. (All GC compounds (Table 1) were screened for in SPMDs). SPMD compounds are only noted in the POCIS column if detected.

Figure 5. Seasonal pesticide detections in POCIS (sand) and water samples (blue) in Folsom during 2013.



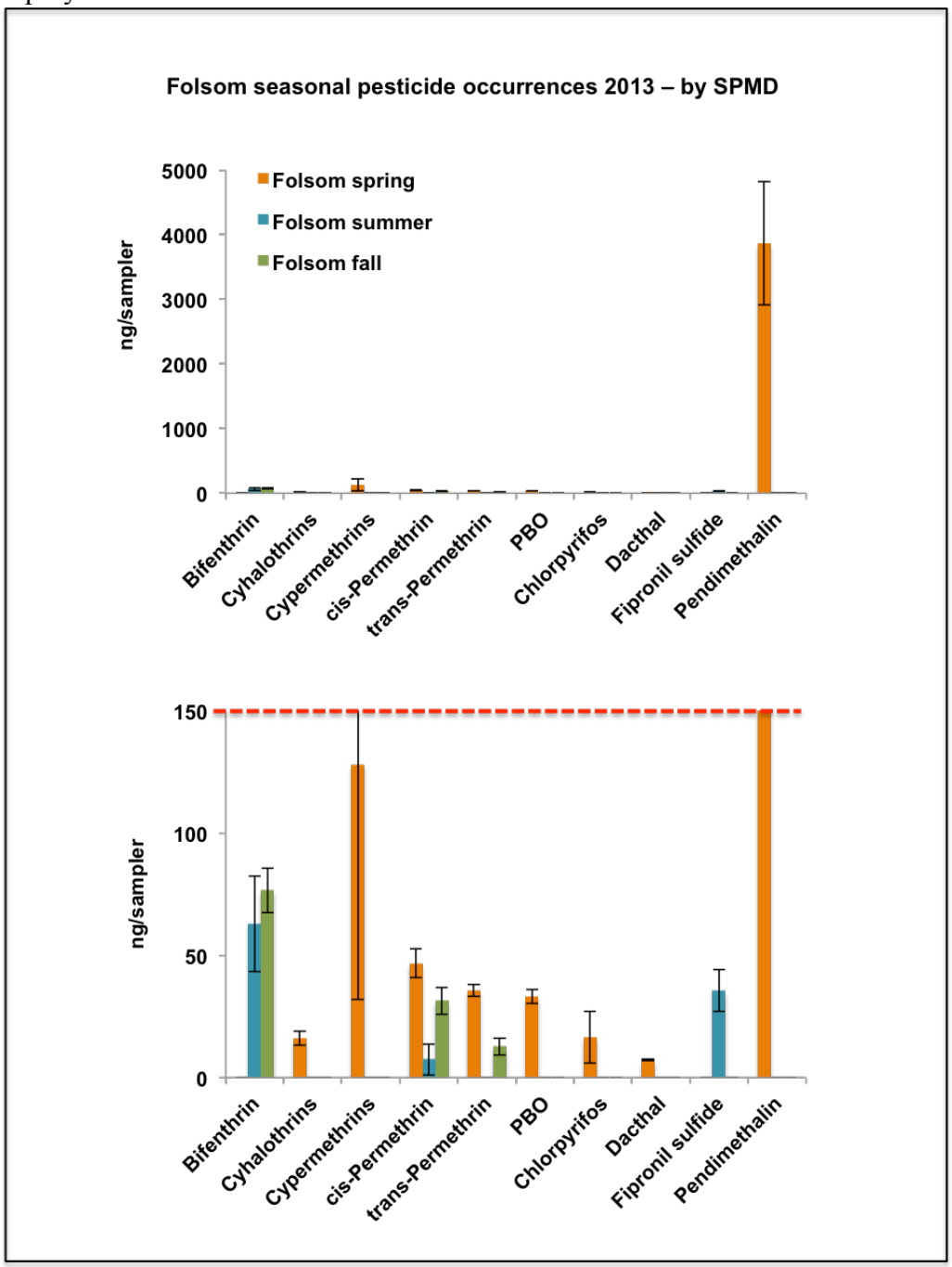
Each column represents a detection (not a concentration). The numbers over the water columns (blue) represent detection frequency (%) based on five grab samples during spring and fall, and 11 composite samples during the summer deployment. The detection frequency only applies to water samples as pesticides measured in the water were not always detected in the sampler. Pesticides are grouped as insecticides, herbicides and fungicides.

Figure 6. Seasonal pesticide detections in POCIS (tan) and water samples (blue) in Salinas during 2013. Pesticides are grouped as insecticides, herbicides and fungicides.



Each column represents a detection (not a concentration). The numbers over the water columns (blue) represent detection frequency (%) based on five grab samples during spring and fall, and 11 composite samples during the summer deployment. The detection frequency only applies to water samples as pesticides measured in the water were not always detected in the sampler. Pesticides are grouped as insecticides, herbicides and fungicides.

Figure 7. Pesticide detections measured in SPMDs in Folsom during the spring, summer and fall deployments of 2013.



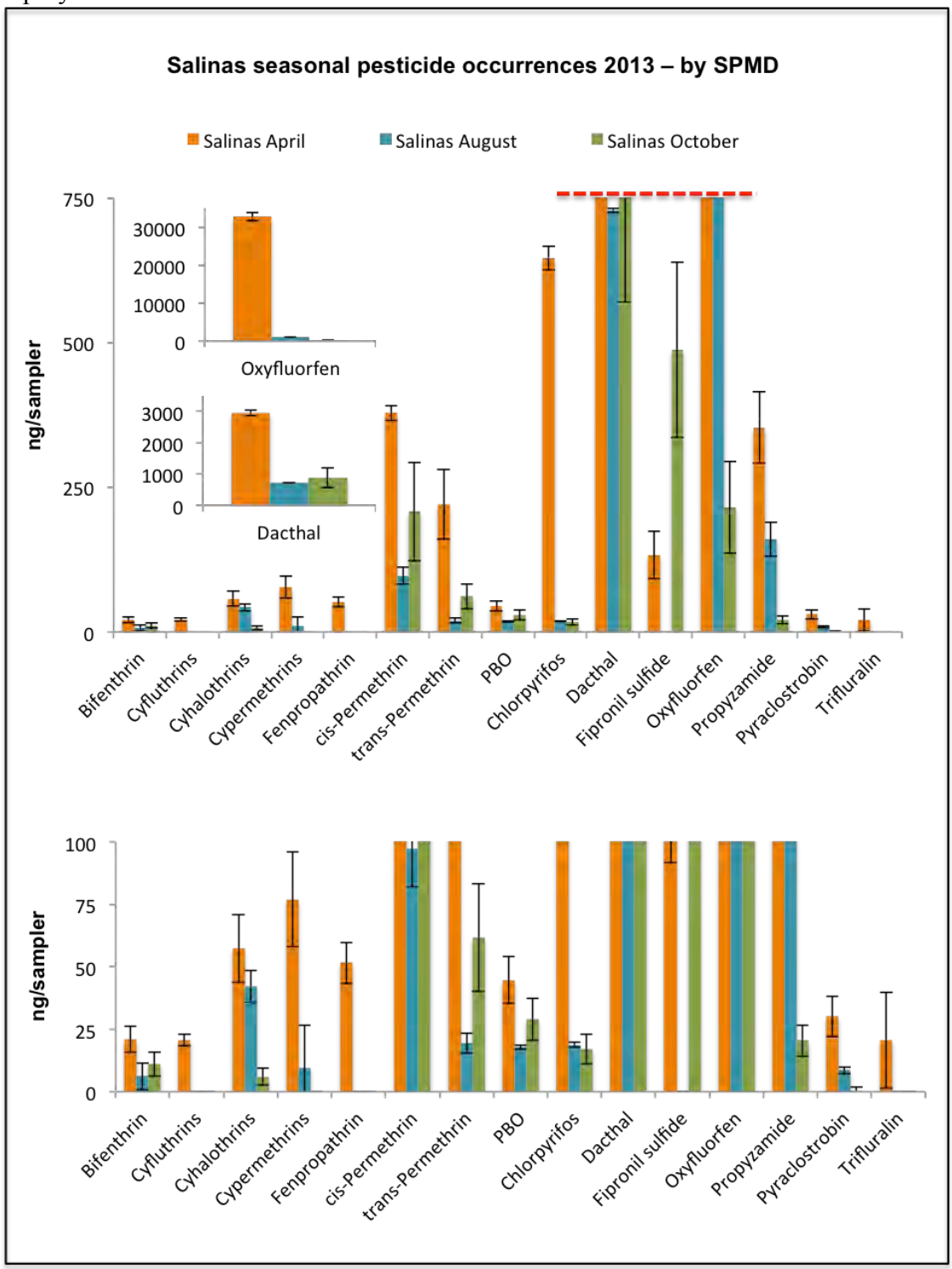
Only pesticides detected in SPMDs in one or more of the three seasons are depicted. Each column represents the mean across 3 replicate samplers. Error bars represent standard deviation. Both plots represent the same data with different y-axis scale. The red line notates full-scale plots for off-axis compounds. Refer to Table 6 for measured concentrations and non-detects of all target pesticides.

Table 6. Summary of pesticide detections in water and SPMDs in Folsom during the spring and summer deployments (Feb/March and July 2013). *Color code: grey (POCIS compounds) and white (SPMD compounds).*

Target pesticide	Target sampler	Water freq. (%) (Spring)	SPMD Concentration (ng/sampler) (Spring)	Water freq. (%) (Summer)	SPMD Concentration (ng/sampler) (Summer)
Diazinon	Both	0	ND	0	ND
Fipronil	POCIS	80	ND	55	ND
Fipronil desulfinyl	POCIS	60	ND	9	ND
Fipronil sulfide	POCIS	0	ND	0	36 (8.7)
Fipronil sulfone	POCIS	60	ND	100	ND
Bifenthrin	SPMD	0	ND	0	63 (20)
Chlorpyrifos	SPMD	0	17 (11)	0	ND
Cyfluthrin	SPMD	0	ND	0	ND
Cyhalothrin	SPMD	0	16 (2.8)	0	ND
Cypermethrin	SPMD	0	128 (96)	0	ND
Dacthal	SPMD	0	7.2 (0.3)	0	ND
Deltamethrin	SPMD	0	ND	0	ND
Esfenvalerate	SPMD	0	ND	0	ND
Fenpropathrin	SPMD	0	ND	0	ND
Metolachlor	SPMD	0	ND	0	ND
Oxyfluorfen	SPMD	0	ND	0	ND
PBO*	SPMD	40	33 (2.9)	0	ND
Pendimethalin	SPMD	80	3,866 (957)	18	ND
Permethrin	SPMD	0	82 (8.3)	18	ND
Prometryn	SPMD	0	ND	0	ND
Propyzamide	SPMD	0	ND	0	ND
Pyraclostrobin	SPMD	0	ND	0	ND
Tebuconazole	SPMD	40	ND	9	ND
Trifluralin	SPMD	0	ND	0	ND

Water freq. refers to detection frequency of composite water samples collected at Folsom 1 throughout the sampler deployment (n=5). Sampler concentrations (mean ± standard deviation) are given for D28 (3 replicate samplers). ND = non-detect (<reporting limit (6 ng/sampler) or <3x blank).

Figure 8. Pesticide detections measured in SPMDs in Salinas during the spring, summer and fall deployments 2013.



Only pesticides detected in SPMDs in one or more of the three seasons are depicted. Each column represents the mean across 3 replicate samplers. Error bars represent standard deviation. All plots represent the same data with different y-axis scale. The inserts show full-scale plots for off-axis compounds (red lines).Tables