SUPPLEMENTAL WATER QUALITY MONITORING FOR ORGANOPHOSPHATE PESTICIDES AND AQUATIC TOXICITY

Central Coast Region Conditional Ag Waiver Cooperative Monitoring Program

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Executive Summary

To fulfill "Follow-up" monitoring requirements in the Central Coast's Conditional Waiver of Waste Discharge Requirements for Discharges from Irrigated Lands (Ag Waiver), organophosphate (OP) pesticides were measured at 23 Cooperative Monitoring Program (CMP) sites in the Lower Salinas and Santa Maria watersheds in August and September, 2006 and again in February and March, 2007. This Follow-up project explored the link between OP pesticides and toxicity to aquatic invertebrates. A group of 7 OP's were detected in Salinas and Santa Maria area water bodies, but results indicated that chlorpyrifos and diazinon were the only OP's present at concentrations likely to impact survival rates of sensitive aquatic invertebrates. Though the relationship was not perfect, a large subset of samples with chlorpyrifos and/or diazinon at or above median lethal concentrations (LC50) for *C. dubia* (water flea) exhibited 100% *mortality* in corresponding toxicity tests. Another large subset of samples with <LC50 concentrations for both chlorpyrifos and diazinon exhibited 100% (or near) *survival* in corresponding *C. dubia* toxicity tests.

Though not a part of a specific Ag Waiver monitoring requirement, the CMP has more recently conducted or collaborated on additional monitoring for pesticides and aquatic toxicity. In September 2007 and September 2008, water samples from the 25 Phase I sites were again analyzed for OP's and aquatic toxicity. The September 2008 effort was a collaborative effort with Dow Agrosciences, and was conducted similarly to the CMP's earlier OP monitoring project, with a few minor differences in site locations to explore areas beyond the CMP's Phase I watersheds. In August 2008, CMP staff collected samples for aquatic toxicity analysis concurrently with sampling for several classes of chemical constituents by the California Department of Pesticide Regulation.

Results of these supplementary pesticide and aquatic toxicity monitoring projects lend further support to many of the conclusions drawn from the CMP's original Follow-up OP monitoring project. For example, the additional monitoring further supports that OP pesticides are fairly ubiquitous at CMP sites in the Salinas and Santa Maria areas, and that only a small subset of OP's are commonly detected. These efforts also support the idea that when chlorpyrifos and/or diazinon are detected at concentrations of known toxicity to aquatic invertebrates, survival rates in corresponding laboratory toxicity tests are typically very low. That said, the supplementary monitoring projects also support the prior conclusion that important exceptions to this pattern exist.

Results of the supplementary pesticide and aquatic toxicity monitoring also suggest some caveats to prior conclusions. For example, in the CMP's original Follow-up OP monitoring project, chlorpyrifos and diazinon were almost exclusively the only OP's found at concentrations likely to impact *C. dubia* survival rates. Supplementary monitoring demonstrated that at some sites, the OP malathion and the carbamate methomyl are also found at concentrations which might impact *C. dubia* survival rates. The additional monitoring conducted in 2008 also provided a small amount of data to suggest that the degree to which pesticides are detected in ambient waters may differ outside of the Lower Salinas and Santa Maria areas. Follow-up monitoring in progress by the CMP in 2009 should provide a stronger dataset to address this question.

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1 INTRODUCTION

To meet requirements of the Conditional Waiver of Waste Discharge Requirements for Discharges from Irrigated Lands (Ag Waiver), the Cooperative Monitoring Program (CMP) began monthly surface water grab sampling at 25 sites in the Lower Salinas and Santa Maria watersheds in January, 2005. (Another 25 sites were added in January, 2006, however the focus of this report is primarily the first 25, or "Phase I" sites.) During monitoring in 2005, several of the 25 sites showed significant, repeated toxicity to invertebrates in water. By that time, several studies had been published linking toxicity observed on the Central Coast to the organophosphate (OP) pesticides chlorpyrifos and diazinon (e.g. Anderson et al. 2003a and b; Hunt et al. 1999; Hunt et al. 2003; Koslowski et al. 2004; Phillips et al. 2004). Both chemicals are commonly applied to crops grown in CMP monitoring areas.

To address Ag Waiver requirements for "Follow-up" monitoring and to further explore the link between OP pesticides and toxicity, OP pesticides were measured in the Phase I monitoring areas concurrently with regularly scheduled CMP water toxicity sampling in August and September, 2006 and again in February and March, 2007 (CCWQP 2008). Measured OP concentrations were compared to published median lethal concentrations (LC50's) for test invertebrates, and then with toxicity observed in concurrently collected water samples. Other relevant metrics are the Central Coast RWQCB "303d-listing" criteria for the protection of aquatic life - 0.025 µg/L and 0.16 µg/L for chlorpyrifos and diazinon, respectively. This project is discussed in detail in CCWQP 2008. Results from the original Phase I Follow-up OP monitoring, in brief, were as follows:

Organophosphates were detected at every site during at least 1 of the 4 sampling events, and at 20 of the sites during at least 2 events. Survival rates for *C. dubia* were significantly reduced in 53% of samples collected, and at least once at 19 of the sites. Of the 19 OP's tested, the following 7 were detected at least once: chlorpyrifos, diazinon, dichlorvos, dimethoate, ethoprop, fenchlorphos, and malathion. Of these, only chlorpyrifos and diazinon were detected at concentrations likely to impact aquatic invertebrate survival rates. There was a strong relationship between *C. dubia* survival rates and the presence of chlorpyrifos and/or diazinon at median lethal concentrations (LC50's) for *C. dubia* (Figure 1). Specifically, a large subset of samples with chlorpyrifos and/or diazinon at or above LC50 concentrations exhibited 100% *mortality* in corresponding *C. dubia* toxicity tests. Another large subset of samples with <LC50 concentrations for both chlorpyrifos and diazinon exhibited 100% (or near) *survival* in corresponding *C. dubia* toxicity tests. It is important to qualify these results, however, as the relationship was not perfect, and no experiments were performed to verify a causal link.

Though not a part of a specific Ag Waiver monitoring requirement, the CMP has more recently conducted or collaborated on additional monitoring for OP's and aquatic toxicity. In September 2007 and September 2008, water samples from the 25 Phase I sites were again analyzed for OP's and aquatic toxicity. The September 2007 effort was identical to the four original Phase I Follow-up OP monitoring events detailed in CCWQP 2008. The September 2008 effort was a collaborative effort with Dow Agrosciences, who were conducting OP monitoring in response to a California Department of Pesticide Regulation (DPR) reevaluation of chlorpyrifos products (Bret and Poletika 2009). This work was conducted similarly to the CMP's original Phase I Follow-up OP monitoring project, with a few minor differences in site locations to explore areas beyond the CMP's Phase I watersheds. Finally, in August 2008, CMP staff collected samples for aquatic toxicity analysis concurrently with sampling for several classes of chemical constituents by DPR staff at 4 sites in the Lower Salinas and Lower Pajaro areas. The monitoring of chemical constituents by DPR was part of a long-term pesticide monitoring effort in progress by DPR in high-use agricultural areas (Starner 2008).

2 METHODS

2.1 Monitoring Approach & Sites

The monitoring approach and sites sampled for the projects discussed in this report were very similar to those in the CMP's original Phase I Follow-up study on OP's and aquatic toxicity (CCWQP 2008). Sample collection in September 2007 was conducted at 15 CMP sites in an agricultural region of northern Monterey County draining to the Salinas River and at 10 sites in an agricultural region on either side of the Santa Maria River near the coast (Table 1; Figure 2). Samples were collected during a regularly scheduled CMP event in September 2007, which was representative of Central Coast late summer or "dry season" conditions. In the August 2008 effort, only four sites were sampled – two in the Lower Salinas/Reclamation Canal area, and two in the Lower Pajaro watershed (Table 1; Figure 3). Sample collection in September 2008 was similar to that in 2007, with some differences in the sites chosen for sampling so as to begin developing information about watersheds outside the Phase I area (Table 1; Figure 4). Sample Collection & Analytical Methods

Water samples for invertebrate toxicity and organophosphate (OP) pesticide analyses were collected from each site on each sampling date. In August 2008, samples were also collected for carbamate and pyrethroid pesticide analysis, and some herbicides. Field sampling and laboratory analytical methods are described in detail in CCWQP 2008 and in the CMP Quality Assurance Project Plan, or "QAPP" (CCWQP 2006). Briefly, ambient water samples were collected from mid-channel at mid-depth by bucket grab. Samples for toxicity analysis were immediately transferred into appropriately cleaned 1-gallon unpreserved amber glass bottles. Samples for pesticide analysis were immediately transferred into appropriately cleaned 1-liter unpreserved amber glass bottles. All samples were transported to the appropriate analytical laboratories on ice, within hold-times, under chain-of-custody.

Organophosphate analyses for the September 2007 and 2008 efforts were conducted by CRG Marine Laboratories (Torrance, CA) using EPA method 625m, gas chromatograpy/mass spectrometry. Analyses for the August 2008 effort (by DPR: organophosphates, carbamates, herbicides, acephate/methamidaphos) were conducted at the Department of Food and Agriculture Center for Analytical Chemistry (methods detailed in Table 5 of Starner 2008). Toxicity analyses were conducted according to US Environmental Protection Agency protocols (USEPA 2002), and consisted of exposing individual females (*Ceriodaphnia dubia*) to ambient waters for the length of time required for control treatment females to produce three broods (typically 6-8 days). After it was determined that ≥60% of *C. dubia* in the control treatments had produced their third brood of offspring, the tests were terminated. Data from the full strength water samples were analyzed and compared to data from the control treatments to evaluate any reductions in survival or reproduction rates attributable to the samples.

2.2 Quality Assurance

Water quality data collected by the CMP are compatible with State of California Surface Water Ambient Monitoring Program (SWAMP) data quality objectives. The CMP also generally follows informal guidance provided by the US EPA regarding data verification and validation.

Quality assurance protocols for the CMP are described in detail in the QAPP, pages 29 – 44 (CCWQP 2006). Field sampling protocols were implemented per the QAPP. In a few cases, the suite of field QA/QC samples collected may differ slightly from standard QAPP prescriptions, due to the limited scope of the projects or programmatic differences between collaborators. Laboratory method blanks, duplicates, and matrix spikes were analyzed to identify contamination and demonstrate precision and accuracy of analytical procedures. Laboratory instruments were calibrated according to a regular schedule and user

manuals where applicable. Additional details regarding quality control for toxicity tests are given in QAPP Appendix B (CCWQP 2006).

3 RESULTS

3.1 Results for September, 2007 Organophosphate and Toxicity Monitoring

3.1.1 Organophosphate results

A total of 20 samples were collected for OP analysis from 18 sites (two sites had duplicate samples) during the sampling event (September 25-26, 2007; Table 3). Sampling was planned for 25 sites, but 3 of the Salinas area sites (Chualar, Gabilan, and Natividad Creeks) and 2 of the Santa Maria area sites (Bradley Canyon Creek and Santa Maria River at Highway 1), did not have flowing water. Organophosphates were detected at every site sampled. Of the 19 OP's for which we tested (Table 2), the following 4 were detected: chlorpyrifos (7 sites), diazinon (13 sites), dimethoate (5 sites), and malathion (12 sites). Of these, chlorpyrifos, diazinon, and malathion were detected at concentrations likely to impact survival rates of sensitive aquatic invertebrates (discussed further in Section 3.1.3, Relationship Between OP's and Toxicity). Site-specific concentrations of each OP compound detected during this sampling event are provided in Table 3.

OP concentrations were reflective of the range of results from the CMP's original Phase I Follow-up OP monitoring events, with the following exceptions:

- Except for the three dry sites, there were no non-detects for diazinon in the Salinas area, with the lowest detection at 0.036 ppb (the range of diazinon levels observed in the CMP's original Follow-up OP monitoring included a few non-detects for this area; the 303d-listing criterion is 0.160 ppb).
- Except for the two dry sites, there were no non-detects for malathion in the Santa Maria area, with the lowest detection at 0.075 ppb (the range of malathion levels observed in the CMP's original Follow-up OP monitoring included some non-detects for this area).
- The highest concentrations for each of the 4 OP's detected in the Salinas area were lower in September 2007 than maximum levels collectively observed during the CMP's original Follow-up OP monitoring.
- The highest concentration of chlorpyrifos in the Santa Maria area was lower in September 2007 than maximum levels collectively observed during the CMP's original Follow-up OP monitoring. The highest diazinon concentration was comparable to prior maximum levels, and the highest dimethoate and malathion levels from September 2007 were much higher than previously observed.

Similarities and differences between these and previous results are presented only in the spirit of qualitative data description. This single monitoring event plus the few others conducted do not make up a sufficient dataset to support trend analysis.

3.1.2 Toxicity results

A total of 19 samples were collected at 18 sites (duplicate samples were collected at 1 site) for analysis of toxicity to *C. dubia*. Three-brood toxicity tests were conducted on samples collected concurrently with each of the OP samples. Survival rates for test organisms were significantly lower than the control in 12 of the 19 samples (11 of 18 sites), or 63% of samples (compare to: 53% of samples from the CMP's original Follow-up OP monitoring events, collectively). Of the 7 samples that did not have significantly

lower survival rates for *C. dubia*, 3 had significantly lower reproduction rates. Site-specific invertebrate survival rates during this sampling event are provided in Table 3.

3.1.3 Relationship between OP's and toxicity

Chlorpyrifos and diazinon have been found to exhibit additive joint acute toxicity to aquatic invertebrates when both are present in water (Bailey et al. 1997). Other OP compounds may behave similarly. It is common to evaluate toxicity, and especially additive toxicity, in terms of *toxic units* (TU's) such that for each compound, 1 TU = median lethal concentration (LC50). Suggested LC50's for each OP detected are given in Table 2; TU's calculated from each OP detection are given with corresponding invertebrate toxicity results in Table 3. In September 2007, samples containing at least 1 TU of OP's comprised 55-58% of the total OP samples collected (11 or 12 samples, depending on how duplicate samples are treated), and an additional 20% of samples contained at least 0.5 TU's (4 samples; Table 3). In prior OP monitoring by the CMP, chlorpyrifos and diazinon were the only OP's detected at >0.2 TU's, with one exception (malathion, 1 sample). In September 2007, malathion was detected in several samples at >0.2 TU's, some of these containing >3 TU's of malathion.

In September 2007, all samples with >1 TU had 100% mortality (0% survival) in corresponding invertebrate toxicity tests. (The samples from Green Valley may have been an exception to this, depending on how duplicate results were treated.) Of the 6 samples with < 1 TU of OP's, only 1 showed significant toxic effects to invertebrate survival rates, and 2 showed significant toxic effects to invertebrate reproduction. One sample with low survival rates had only 0.1 OP-related TU, raising the question of what other chemical classes may have been present in the sample.

3.2 Results for August, 2008 Pesticide and Toxicity Monitoring (collaborative effort with Department of Pesticide Regulation)

Sampling by DPR for chemical constituents was part of DPR Study 252: Long-term Pesticide Monitoring in High-Use Agricultural Areas: Year Two, Central Coast and Imperial Valley (Starner 2008). More information on that project is available in PDF format on DPR's website: http://www.cdpr.ca.gov/docs/emon/surfwtr/protocols/study252protocol.pdf.

3.2.1 Pesticide results

A total of 6 samples were collected for analysis of OP's (including acephate and methamidaphos), carbamate pesticides, and a group of herbicides during the sampling event (August 19, 2008; Table 2). Sampling was conducted at 4 sites – Salinas Reclamation Canal near Airport Blvd., Tembladero Slough at Haro, Pajaro River at Thurwachter Bridge, and Watsonville Slough at Shell Rd. The Reclamation Canal and Tembladero Slough sites were sampled in both the morning and afternoon.

None of the compounds analyzed were found at either of the Pajaro area sites. Chlorpyrifos, diazinon, dimethoate and a carbamate – methomyl – were detected in all samples from the Salinas area sites. The other OP's detected – dichlorvos and malathion – were found only in Tembladero Slough (in trace amounts, too small to be quantified). The herbicide active ingredients oryzalin and oxyfluorfen were found only in Tembladero Slough. At the two Salinas area sites, which were sampled in both the morning and afternoon, there were no strong patterns with regard to morning versus afternoon concentrations. Site-specific pesticide results are provided in Table 4.

3.2.2 Toxicity results

A total of 7 samples were collected at the 4 sites (1 site had duplicates; 2 sites were visited twice) for analysis of toxicity to *C. dubia* and *Pimephales* (fathead minnow). Toxicity tests were conducted on samples collected concurrently with the pesticide/herbicide samples. Results showed no toxicity to

Pimephales at any of the sites. Survival rates for *C. dubia* were significantly lower than the control in both morning and afternoon samples from the Salinas Reclamation Canal. No toxicity was observed (neither survival nor reproduction) at any of the other three sites. A sub-lethal endpoint for invertebrates could not be assessed at the Pajaro River (Thurwachter Bridge) site due to use of an alternative test species (*Hyalella azteca*) because of high salinity. Site-specific toxicity results are provided in Table 4.

3.2.3 Relationship between pesticides and toxicity

Toxic Units in this report are calculated based on literature LC50 values, which vary depending on the specific organism, chemical, toxicity test duration, and chronic versus acute test type. The DPR Study 252 (Starner 2008) cites effects levels from a US EPA aquatic life benchmark table (US EPA 2007; this table has since been updated by the EPA), which is based on the most sensitive, scientifically acceptable toxic endpoints identified by the EPA for a given taxon (i.e. "aquatic invertebrates," not necessarily *C. dubia*). For the sake of consistency, and also because the exact species in the EPA table are not readily discernable, the following discussion of TU's is based on the LC50's previously used and cited in Table 2 of this report. In several cases, the toxic endpoint values cited in the EPA table are lower than the LC50's used here. Also, the carbamate methomyl was not previously analyzed in a CMP study, so the benchmark for acute toxicity to invertebrates from DPR Study 252 Table 2 – 4.4 µg/L – is used here (Starner 2008).

In August 2008, all samples with chemical detections contained at least 0.6 TU's (aggregate) of the detected constituents (all morning and afternoon samples from the Salinas Reclamation Canal and Tembladero Slough; Table 4). If the trace detections of dichlorvos and malathion are included at the level of their reporting limits (0.05 and 0.04 ug/L, respectively), then all samples with chemical detections contained >1 TU, but this may be an overrepresentation of the actual concentrations present. Diazinon contributed to the TU count more than any other parameter. Despite the fact that both Tembladero Slough samples contained measurable TU's (0.6 to 1.1, depending on how trace detections are treated), neither exhibited toxicity to invertebrates (survival or reproduction). Results from the Salinas Reclamation Canal were more predictable – these contained 1.4 to 1.8 TU's, and both samples had 0% survival rates for *C. dubia*. The Pajaro River and Watsonville Slough sites had no measured TU's, 100% survival rates, and Watsonville Slough had a 96% reproduction rate relative to the control.

3.3 Results for September, 2008 Organophosphate and Toxicity Monitoring (collaborative effort with Dow Agrosciences)

Sampling by Dow Agrosciences for OP's in 2008 was a field investigation of chlorpyrifos exceedances in surface water, undertaken in response to a DPR reevaluation of chlorpyrifos products. The Dow Agrosciences report on this study was recently released – Historical Trend Analysis and Field Investigations of Chlorpyrifos Exceedances in Surface Water (Brett and Poletika 2008). This report is available upon request from the DPR.

3.3.1 Organophosphate results

A total of 21 samples were collected at 21 sites for OP analysis during the sampling event (September 23 – October 2, 2007). Sampling was planned for 23 sites, but 2 of the Salinas River sites (at Spreckles and Chualar) did not have flowing water. Sampling sites were generally the same as in the September, 2007 event and in the CMP's original Phase I Follow-up OP monitoring efforts. However, to improve spatial coverage, several sites in the Salinas and Santa Maria areas were replaced with sites from the Pajaro River, Santa Ynez River, and Santa Barbara area creeks (Table 1; Figure 4).

Organophosphates were detected at every site in the Salinas and Santa Maria areas (Table 5). Outside of those areas, the only OP detection was in San Juan Creek (diazinon, 0.017 ppb). Of the 19 OP's for which we tested (Table 2), the following 6 were detected: chlorpyrifos (10 sites), diazinon (15 sites),

dichlorvos (3 sites), dimethoate (11 sites), ethoprop (1 site), and malathion (12 sites). Of these, only chlorpyrifos, diazinon, and in one case malathion, were detected at concentrations likely to impact survival rates of sensitive aquatic invertebrates (discussed further in Section 3.3.3). Site-specific concentrations of each OP compound detected during this sampling event are provided in Table 5.

OP concentrations were somewhat reflective of the range of results from the CMP's original Phase I Follow-up OP monitoring events in some cases, but there were numerous exceptions to this:

- In the Salinas area, maximum chlorpyrifos and diazinon concentrations were less than maximum levels observed in prior efforts
- Dichlorvos was detected in the Salinas area (it had not been before)
- Maximum concentrations of dimethoate and malathion were higher in the Salinas area than in previous efforts
- In the Santa Maria area, the maximum chlorpyrifos concentration was less than the maximum level observed in prior efforts
- Maximum concentrations of diazinon, dichlorvos, dimethoate, and malathion were higher in the Santa Maria area than in previous efforts (though only slightly in some cases)
- Ethoprop was detected in the Santa Maria area (it had not been before)

Similarities and differences between these and previous results are presented only in the spirit of qualitative data description. This single monitoring event plus the few others conducted prior do not make up a sufficient dataset to support trend analysis.

3.3.2 Toxicity results

A total of 25 samples were collected at 21 sites (4 sites had duplicates) for analysis of toxicity to *C. dubia*. Three-brood toxicity tests were conducted on samples collected concurrently with each of the OP samples. Survival rates for test organisms were significantly lower than the control in 14 of the 25 samples (12 of 21 sites), or 56% of samples. These samples were all from the Salinas and Santa Maria areas. Of the 11 samples that did not have significantly lower survival rates for *C. dubia*, 7 were tested for reproductive effects (4 were samples with higher salinities, requiring an alternative test species for which reproductive endpoint testing is not part of the protocol). All of these samples had significantly lowered reproduction rates. Site-specific invertebrate survival and reproduction rates during this sampling event are provided in Table 5.

3.3.3 Relationship between OP's and toxicity

In September 2008, samples containing at least 1 toxic unit (TU) of OP's comprised 43% of the total OP samples collected (9 samples), and an additional 14% contained at least 0.5 TU's (3 samples; Table 5). As in other monitoring events, chlorpyrifos, diazinon, and malathion were the only OP's detected in amounts which measurably contributed to the TU count.

In September 2008, all but two samples with >1 TU had 100% mortality (0% survival) in corresponding invertebrate toxicity tests. One of the two samples which did not have 100% mortality had only 50% survival (significant toxic effect), and the other had >100% survival relative to the control. This latter sample (from Orcutt-Solomon Creek at Highway 1) had exactly 1 OP-related TU, calculated based on *C. dubia* LC50's. Due to high specific conductance in the sample water, an alternative test species (*Hyalella azteca*) was used for the test. *Hyalella* is somewhat less sensitive to OP's than *C. dubia*, so it is possible that the high survival rate was due to the use of this alternative test species. Of the 12 samples with < 1 TU of OP's, 5 showed significant toxic effects to invertebrate survival rates (these had from 0 to 0.9 OP-related TU's). Six others showed significant toxic effects to invertebrate reproduction (these had from 0 to 0.6 OP-related TU's). One of the samples with significantly lowered survival rates and 2 of the

samples with significantly lowered reproduction rates had no OP-related TU's, raising the question of what other chemical classes may have been present in the sample.

4 DISCUSSION & CONCLUSIONS

Together, the monitoring efforts detailed in this report reaffirm some of the major conclusions of the CMP's original Phase I Follow-up OP and toxicity monitoring. For example:

- OP pesticides are fairly ubiquitous at CMP sites in the Salinas and Santa Maria areas.
- Though samples can be analyzed for a broad spectrum of OP products, only a small subset (4 or 5) are commonly detected, and only a slightly larger subset (6 or 7) are ever detected, at least by the CMP.
- Chlorpyrifos and diazinon are the OP's most commonly detected at levels known to be toxic to the aquatic invertebrate, *Ceriodaphnia dubia*.
- When chlorpyrifos and/or diazinon are detected at concentrations of known toxicity to aquatic invertebrates, survival rates in corresponding laboratory toxicity tests are typically very low. (There are important exceptions to this pattern, however.)

Some additional conclusions may also be drawn, based on new information from the efforts discussed in this report:

- At certain sites in agricultural watersheds outside the Salinas and Santa Maria areas, OP's and other pesticides are not detected as consistently. The sample size from the efforts discussed in this report is too small to draw firm conclusions, however additional OP monitoring by the CMP in 2009 should serve to confirm or refute this observation.
- The OP malathion is present at many CMP sites, sometimes at levels known to be toxic to aquatic invertebrates, or at levels which contribute measurably to calculations of total TU's. (This was almost never the case in prior monitoring by the CMP.)
- The carbamate methomyl is also sometimes present at levels which can contribute measurably to calculations of total TU's.

It is also important to consider streamflow (discharge) in this discussion. In some cases, for example the Pajaro River at Main St., flows were high but no OP's were detected. At other sites, for example Quail Creek, OP concentrations were high relative to some other sites, but flows were very low (< 0.1 CFS). There were also a few sites with both high flows and high relative OP concentrations, for example Orcutt-Solomon Creek near the mouth and the Santa Maria River just downstream at the estuary. In watersheds where a large portion of flows are comprised of irrigation-related discharges, efforts by growers to reduce tailwater volumes should result in flow reductions at the bottom of the watershed. Though OP concentrations at levels toxic to aquatic invertebrates will continue to have localized toxic effects, reduced flows will reduce loads to downstream water bodies.

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Tables

Table 1. Station names and locations for CMP projects pairing monitoring for aquatic toxicity and monitoring for specific chemical constituents.

Site Description	Site ID	Longitude	Latitude	'06 / '07 Follow-up	Sept 2007	Aug '08 w/ DPR	Sept '08 w/ Dow
LOWER SALINAS WATERSHED							
Moro Cojo Slough at Highway 1	306MOR	-121.78328	36.79646	■	■		
Salinas Reclamation Canal, La Guardia	309ALG	-121.61297	36.65697	■	■	■*	■
Alisal Slough at White Barn	309ASB	-121.72968	36.72482	■	■		
Blanco Drain Below Pump	309BLA	-121.74393	36.71060	■	■		■
Chualar Creek at Chualar River Road	309CRR	-121.50995	36.56142	■	■		■**
Espinosa Slough u/s Alisal Slough	309ESP	-121.73372	36.73675	■	■		■
Gabilan Creek at Boronda Road	309GAB	-121.61641	36.71548	■	■		
Salinas Rec. Canal at San Jon Road	309JON	121.70496	36.70493	■	■		■
Merritt Ditch u/s Highway 183	309MER	-121.74168	36.75158	■	■		
Natividad Creek u/s Salinas Rec. Canal	309NAD	-121.60197	36.70254	■	■		■
Old Salinas R. at Monterey Dunes Way	309OLD	-121.787855	36.772291	■	■		
Quail Creek at Highway 101	309QUI	-121.56211	36.60943	■	■		■
Salinas R. at Chualar Bridge, River Rd.	309SAC	-121.547737	36.553757	■	■		■
Salinas River at Spreckels Gauge	309SSP	-121.67339	36.62967	■	■		■
Tembladero Slough at Haro	309TEH	-121.75445	36.75952	■	■	■	■
SANTA MARIA WATERSHED							
Bradley Channel at Culvert	312BCC	-120.37399	34.94507	■	■		■
Bradley Channel at Jones Street	312BCJ	-120.41679	34.94544	■	■		■
Green Valley at Simas	312GVS	-120.556457	34.942280	■	■		■
Main St. Canal u/s Ray Rd at Hwy 166	312MSD	-120.486578	34.955227	■	■		■
Oso Flaco Creek at Oso Flaco Lake Rd.	312OFC	-120.586259	35.016388	■	■		■
Little Oso Flaco Creek	312OFN	-120.586157	35.022795	■	■		
Orcutt Solomon Creek at Highway 1	312OR1	-120.572882	34.941374	■	■		■
Orcutt Solomon Crk u/s Santa Maria R.	312ORC	-120.631454	34.957554	■	■		■
Santa Maria River at Highway 1	312SM1	-120.569832	34.977207	■	■		
Santa Maria River at Estuary	312SMA	-120.641796	34.963774	■	■		■
OTHER WATERSHEDS							
San Juan Crk, Anzar Rd. (upper Pajaro)	305SJA	-121.56141	36.87536				■
Pajaro R. (lower), Thurwachter Bridge	305THU	-121.79306	36.87972			■	
Pajaro R. (lower), Main St.	305PJP	-121.75114	36.90518				■
Watsonville Slough, Shell Rd.	--	-121.81833	36.87111			■	
Santa Ynez River at 13th St.	314SYN	-120.55442	34.67677				■
Bell Creek at Winchester Park	315BEF	-119.90612	34.43844				■
Franklin Creek at Mountain View	315FMV	-119.51733	34.40693				■

* DPR sampling site at Airport Blvd. ** Dow sampling site downstream, incorporating ~60% more drainage area..

Table 2. Specific chemical constituents analyzed concurrently with toxicity samples for supplementary projects. Method detection and reporting limits are also provided. Units for organophosphates are µg/L. Median lethal concentrations (LC50) are given for 6 of the 7 organophosphates detected in CMP studies (in µg/L). Asterisk * indicates detected chemical.

Water Quality Parameter	Method Detection Limit	Reporting Limit	LC50's, *303d Criteria*
ORGANOPHOSPHATES - ALL PROJECTS EXCEPT 08/2008 WITH DPR			
Chlorpyrifos*	0.001	0.002	0.053 [1], *0.025*
Demeton	0.001	0.002	--
Diazinon*	0.002	0.004	0.32 [1], *0.16*
Dichlorvos*	0.003	0.006	0.149 [2]
Dimethoate*	0.003	0.006	600 [3]
Disulfoton	0.001	0.002	--
Ethoprop*	0.001	0.002	--
Fenchlorphos*	0.002	0.004	1.8 [4]
Fensulfothion	0.001	0.002	--
Fenthion	0.002	0.004	--
Malathion*	0.003	0.006	1.1 to 3.2 [5]
Merphos	0.001	0.002	--
Methyl Parathion	0.001	0.002	--
Mevinphos	0.008	0.016	--
Phorate	0.006	0.012	--
Sulprofos	0.002	0.004	--
Tetrachlorvinphos	0.002	0.004	--
Tokuthion	0.003	0.006	--
Trichloronate	0.001	0.002	--
ANALYTES FROM 08/2008 SAMPLING WITH DPR			
Organophosphates by GC/FPD	*Carbamates by LCMS*	*Herbicides by LC/MS/MS*	
Chlorpyrifos*, Diazinon*, Dichlorvos*, Dimethoate*, Disulfoton, Ethoprop, Fenamiphos, Fonofos, Malathion*, Methidathion, Methyl Parathion, Phorate, Profenfos (Acephate/Methamidaphos by separate analysis)	Aldicarb SO Aldicarb SO2 Oxamyl Methomyl* 3-OH Carbofuran Aldicarb Carbofuran Carbaryl Mesurol	Oryzalin* Ethalfluralin Trifluralin Benfluralin Prodiamine Pendimethalin Oxyfluorfen*	
Analytical method details for all DPR constitutents available at http://www.cdpr.ca.gov/docs/emon/surfwtr/protocols/study252protocol.pdf			
TOXICITY-RELATED PARAMETERS, FROM ALL PROJECTS			
Invertebrate Toxicity, Survival	Results reported as survival, growth, or reproduction rates as % of control (0 to >100%). Minimum reportable result = 0%, regardless of actual toxic strength of sample.		
Invertebrate Toxicity, Reproduction			
Fish Toxicity, Survival			
Fish Toxicity, Growth			

Notes:

* Indicates chemicals detected

1 LC50 ref., chlorpyrifos and diazinon: Bailey et al. 1997

2 LC50 ref., dichlorvos: Brooke 1991

3 LC50 ref. (*Daphnia magna*), dimethoate: Beusen and Neven 1989

4 LC50 ref. (Daphnia magna), fenchlorphos: Frear and Boyd 1967

5 LC50 ref., malathion: Nelson and Roline 1998

6 LC50 ref., unionized ammonia: Ankley et al. 1990

Table 3. Organophosphates detected and laboratory aquatic toxicity test results from the September, 2007 monitoring effort.

Monitoring Site Description	Monitoring Site ID	Chlorpyrifos	Diazinon	Dimethoate	Malathion	Total OP-related Toxic Units	Invertebrate Survival Rate	Invertebrate Reproduction Rate	Flow (CFS)
Moro Coho Slough at Highway 1	306MOR	ND	0.036	ND	ND	0.1	92	100	-0.4
Salinas Reclamation Canal at La Guardia	309ALG	ND	*0.317*	ND	ND	1.0	*0*	0	1.0
Alisal Slough at White Barn	309ASB	ND	*0.204*	ND	ND	0.6	100	not assessed	0.8
Blanco Drain below Pump	309BLA	0.010	0.141	0.032	0.027	0.6	90	*69*	4.5
Espinosa Slough upstream from Alisal Slough	309ESP	ND	*0.166*	ND	0.079	0.6	90	*70*	0.3
Salinas Reclamation Canal at San Jon Road	309JON	ND	*0.484*	0.144	0.081	1.6	*0*	0	1.8
Merrit Ditch upstream from Highway 183	309MER	ND	*0.187*	0.325	ND	0.6	100	127	0.7
Old Salinas River at Monterey Dunes Way	309OLD	ND	0.037	ND	ND	0.1	*0*	not assessed	-1.6
Quail Creek at Highway 101	309QUI	*0.048 / 0.053*	0.058 / *0.647*	ND	ND	1.1 to 3.0	*0 / 0*	0 / 0	0.8
Tembladero Slough at Haro	309TEH	ND	*0.365*	0.187	0.080	1.2	*0*	11	6.7
Bradley Channel at Jones Street	312BCJ	*0.225*	ND	ND	0.119	4.4	*0*	22	1.0
Green Valley at Simas	312GVS	*0.029 / 0.039*	ND	ND	0.104 / 0.107	0.6 to 1.1	90	*53*	1.4
Main Street Canal u/s Ray Road at Highway 166	312MSD	ND	ND	ND	0.236	0.2	100	104	0.4
Oso Flaco Creek at Oso Flaco Lake Road	312OFC	ND	ND	0.485	*5.050*	4.6	*0*	0	3.2
Little Oso Flaco Creek	312OFN	ND	ND	ND	*4.109*	3.7	*0*	0	1.0
Orcutt Solomon Creek at Highway 1	312OR1	*0.036*	0.069	ND	0.075	1.0	*67*	not assessed	5.3
Orcutt Solomon Creek u/s Santa Maria River	312ORC	*0.301*	*0.401*	ND	0.344	7.2	*0*	0	11.1
Santa Maria River at Estuary	312SMA	*0.288*	*0.381*	ND	0.371	7.0	*0*	0	11.0

All OP concentrations are given in parts per billion (ppb, or µg/L). Total OP-related TU's were calculated based on values in Table 2. Invertebrate survival and reproduction rates are given as %, relative to the control. Flows are instantaneous discharge measurements collected via cross-channel velocity/depth transect at the time of sampling for OP's and toxicity. "ND" = "not detected." *Italic* text denotes OP concentrations above CCRWQCB 303d-listing criteria (0.025 µg/L for chlorpyrifos; 0.160 µg/L for diazinon), malathion above literature LC50 values, or Invertebrate Toxicity results determined to be "toxic" (significantly lower than control performance).

Table 4. Pesticide and herbicide detections and laboratory aquatic toxicity test results from the August, 2008 monitoring effort. This effort was conducted in collaboration with the Department of Pesticide Regulation.

Monitoring Site Description (ID)	Time	Chlorpyrifos	Diazinon	Dichlorvos	Dimethoate	Malathion	Methomyl	Total Measured Toxic Units	Invertebrate Survival Rate	Invertebrate Reproduction Rate
Tembladero Slough at Haro (309TEH)*	10:45 AM	0.018	0.060	< 0.05	0.197	< 0.04	0.462	0.6 to 1.0**	100	93
	2:45 PM	*0.046*	0.054	ND	0.107	< 0.04	0.280	1.1	100	109
Salinas Rec. Canal at Airport Blvd. (near 309ALG)	10:00 AM	*0.031*	*0.323*	ND	0.244	ND	1.004	1.8	*0*	0
	4:00 PM	*0.025*	*0.214*	ND	0.281	ND	0.915	1.4	*0*	0
Pajaro River at Thurwachter Bridge (305THU)	12:00 PM	None of the measured chemical constituents were detected							91	not assessed
Watsonville Slough at Shell Rd. (near 305WSA)	1:30 PM	None of the measured chemical constituents were detected							100	96

All concentrations are given in parts per billion (ppb, or µg/L). Invertebrate survival and reproduction rates are given as %, relative to the control. "ND" = "not detected." *Italics* denotes OP concentrations above CCRWQCB 303d-listing criteria (0.025 µg/L for chlorpyrifos; 0.160 µg/L for diazinon), other OP's above literature LC50 values, or Invertebrate Toxicity results determined to be "toxic" (significantly lower than control performance). Total TU's related to the constituents measured were calculated based on values in Table 2 and from DPR Study 252 (Starner 2008). Concentrations used in TU calculations were as follows: 1 TU chlorpyrifos = 0.053 µg/L; 1 TU diazinon = 0.320 µg/L; 1 TU dichlorvos = 0.149 µg/L; 1 TU dimethoate = 600 µg/L; 1 TU malathion = 1.1 µg/L; 1 TU methomyl = 4.4 µg/L. The most appropriate concentrations for use in such calculations will change as more studies determining LC50's for specific chemistries and specific organisms are published.

* The herbicide active ingredients Oryzalin and Oxyfluorfen were also detected in the Tembladero Slough as follows: Oryzalin at 0.656 and 0.367 µg/L in morning and afternoon, respectively; Oxyfluorfen at 0.143 and 0.160 µg/L in morning and afternoon, respectively.

** TU calculations are higher if "trace" detections are included at the reporting limit value.

Table 5. Organophosphates detected and laboratory aquatic toxicity test results from the August, 2008 monitoring effort. This effort was conducted in collaboration with Dow Agrosciences.

Monitoring Site Description	Monitoring Site ID	Chlorpyrifos	Diazinon	Dichlorvos	Dimethoate	Ethoprop	Malathion	Total OP-related Toxic Units	Invertebrate Survival Rate	Invertebrate Reproduction Rate	Flow (CFS)
Pajaro River at Main St.	305PJP	ND	ND	ND	ND	ND	ND	0.0	*10*	1	10.7
San Juan Creek at Anzar Rd.	305SJA	ND	0.017	ND	ND	ND	ND	0.1	96	not assessed	0.2
Salinas Reclamation Canal at La Guardia	309ALG	ND	*0.180*	ND	3.288	ND	ND	0.6	*0 / 0*	17 / 22	0.1
Blanco Drain below Pump	309BLA	ND	0.047	ND	0.018	ND	ND	0.1	100	*3*	1.7
Chualar Creek at Highway 101	309CRR	*0.041*	0.090	ND	ND	ND	0.036	1.1	*50*	34	0.0
Espinosa Slough u/s from Alisal Slough	309ESP	ND	0.099	ND	0.068	ND	0.017	0.3	*0*	not assessed	0.0
Salinas Reclamation Canal at San Jon Rd	309JON	ND	0.101	ND	0.066	ND	ND	0.3	100 / 100	*85 / 86*	1.9
Natividad Creek at Constitution Ave	309NAD	ND	0.026	0.083	ND	ND	*1.632*	2.1	*0*	0	0.0
Quail Creek at Highway 101	309QUI	*0.031*	*1.166*	ND	0.094	ND	0.026	4.3	*0*	0	0.0
Tembladero Slough at Haro	309TEH	ND	0.088	ND	0.210	ND	ND	0.3	100	*66*	0.0
Bradley Canyon Creek	312BCC	0.022	0.021	0.007	0.050	0.011	0.024	0.6	90	*73*	0.0
Bradley Channel at Jones Street	312BCJ	*0.109*	0.036	0.112	ND	ND	0.060	3.0	*0*	0	0.3
Green Valley at Simas	312GVS	*0.180*	ND	ND	ND	ND	0.024	3.4	*0*	1	1.5
Main Street Canal u/s Ray Rd at Hwy 166	312MSD	0.018	0.021	ND	ND	ND	0.502	0.9	*0*	0	0.4
Oso Flaco Creek at Oso Flaco Lake Road	312OFC	0.014	ND	ND	0.024	ND	0.902	1.1	*0 / 0*	0 / 0	2.5
Orcutt Solomon Creek u/s Santa Maria River	312ORC	*0.562*	*0.249*	ND	0.256	ND	0.008	11.4	*0*	0	8.5
Orcutt Solomon Creek at Highway 1	312ORI	*0.049*	0.013	ND	1.518	ND	0.028	1.0	102	not assessed	5.2
Santa Maria River at Estuary	312SMA	*0.416*	*0.481*	ND	0.212	ND	0.020	9.4	*0*	0	7.4
Santa Ynez River at 13th Ave.	314SYN	ND	ND	ND	ND	ND	ND	0.0	90	*75*	0.0
Bell Creek at Winchester	315BEF	ND	ND	ND	ND	ND	ND	0.0	102 / 104	not assessed	0.1
Franklin Creek at Mountain View	315FMV	ND	ND	ND	ND	ND	ND	0.0	111	*50*	0.1

All OP concentrations are given in parts per billion (ppb, or ug/L). Total OP-related TU's were calculated based on values in Table 2. Invertebrate survival and reproduction rates are given as %, relative to the control. Flows are instantaneous discharge measurements collected via cross-channel velocity/depth transect at the time of sampling for OP's and toxicity. "ND" = "not detected." *Italics* denotes OP concentrations above CCRWQCB 303d-listing criteria (0.025 µg/L for chlorpyrifos; 0.160 µg/L for diazinon), other OP's above literature LC50 values, or Invertebrate Toxicity results determined to be "toxic" (significantly lower than control performance).

Figures

Figure 1. Relationship between joint OP-related toxic units (TU's) and observed toxicity to aquatic invertebrates in original CMP Phase I Follow-up OP monitoring project (CCWQP 2008). (Toxic units were derived from OP concentrations measured and the published LC50 values given in Table 2.) One outlier (105 OP-related TU's and 0% survival) has been omitted to improve readability of the graph. The dashed line delineates results greater and less than 1 OP-related TU.

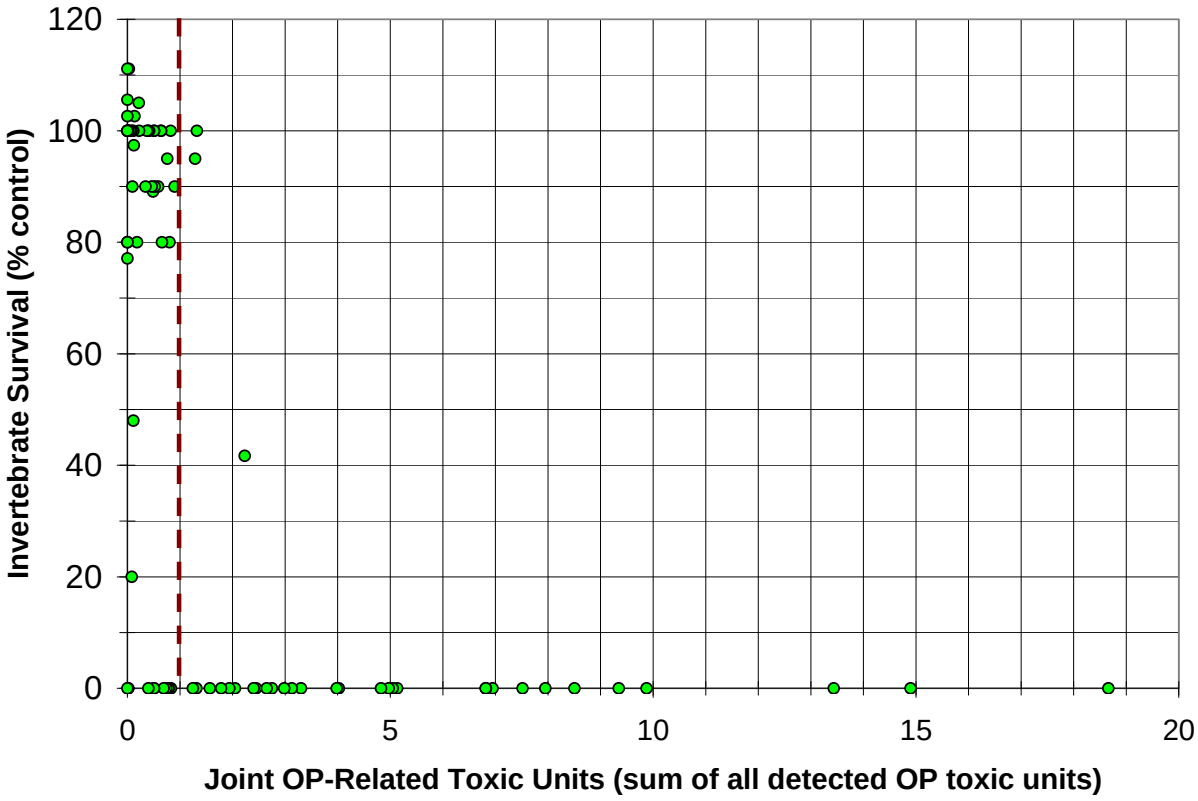

Figure 2. Organophosphate and aquatic toxicity monitoring sites from original Phase I Follow-up OP monitoring efforts (August and September 2006; February and March 2007), and from the September, 2007 event detailed in this report. a) Santa Maria area sites. b) Lower Salinas area sites.

a)

b)

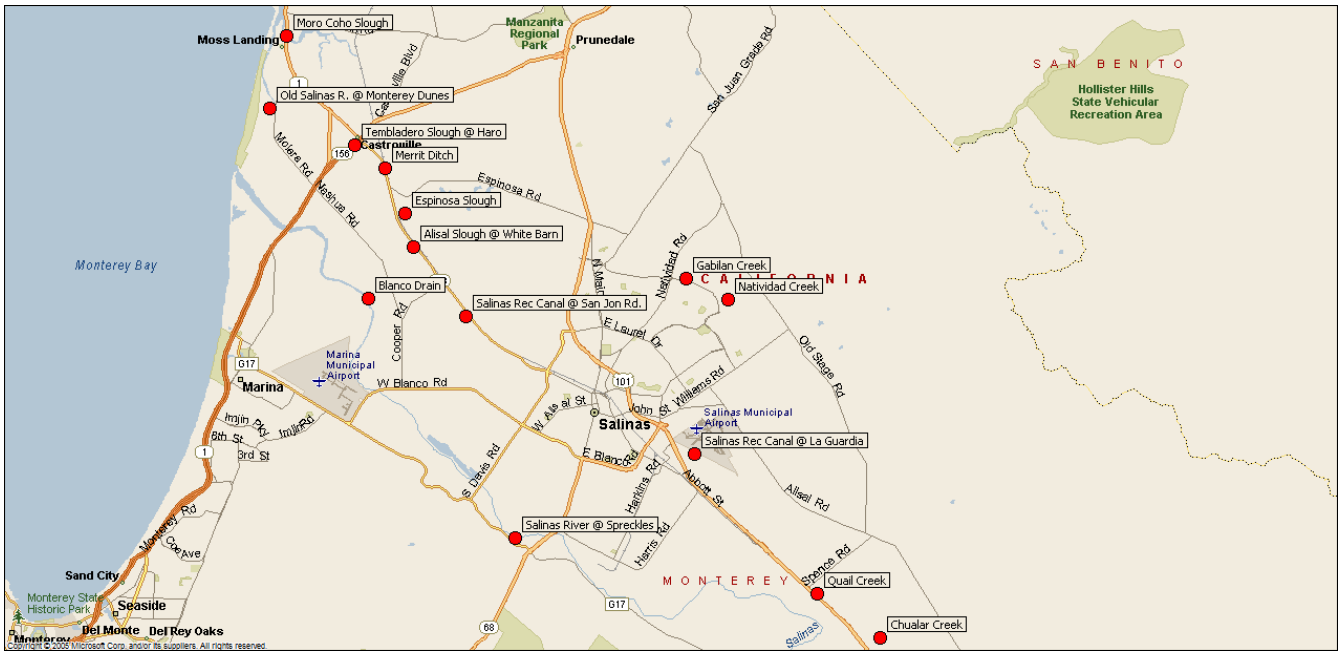

Figure 3. Pesticide and aquatic toxicity monitoring sites from the collaborative monitoring effort with Department of Pesticide Regulation, August 2008. a) Pajaro River sites. b) Salinas area sites.

a)

b)

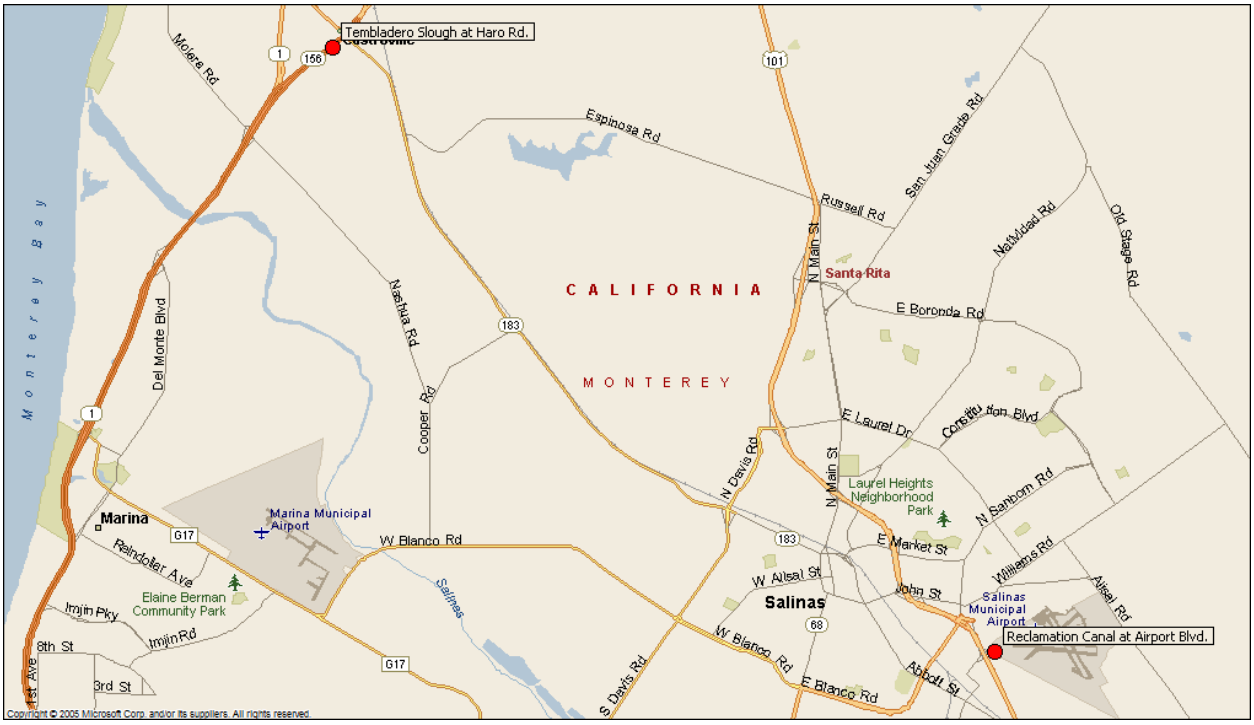

Figure 4. Organophosphate and aquatic toxicity monitoring sites from the September 2008 collaborative effort with Dow Agrosciences. Shown here are only those sites which were outside of the CMP's original Phase I Follow-up OP monitoring areas. All other sites monitored in September 2008 were within the original Phase I study area show in Figure 2.) a) Pajaro sites. b) Santa Barbara sites.

a)

b)