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Detections of Eleven Organophosphorus Insecticides and One Herbicide Threatening Pacific Salmonids, *Oncorhynchus* spp., in California, 1991–2010

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Abstract California's surface water monitoring results from 1991 through 2010 were analyzed to determine whether 12 organophosphorus insecticides and herbicides (i.e., azinphos methyl, bensulide, dimethoate, disulfoton, ethoprop, fenamiphos, methamidophos, methidathion, methyl parathion, naled, phorate, and phosmet) and their degradates have been detected above maximum concentration limits (MCLs) in Pacific salmonid habitats. Methidathion, methyl parathion, phorate, phosmet, and the oxygen analogue of naled (DDVP) detections exceeded MCLs. Methyl parathion detections may be accounted for by monthly use trends, while methidathion detections may be explained by yearly use trends. There were inadequate phorate, phosmet, or DDVP data to evaluate for correlations with use.

Keywords Organophophorus · Surface water · Salmonids · Endangered species

Many anthropogenic and natural factors have contributed to the listing of 28 Pacific anadromous salmonid groups (salmon) as threatened or endangered under the Endangered Species Act (ESA) since 1991 (Rumsey 2009). The Biological Opinion required by the National Marine Fisheries Service under the ESA investigated the active ingredients of 11 organophosphorus insecticides and 1 organophosphorus herbicide as well as their degradates. National Marine Fisheries Service analyzed their likelihood of reducing the survival, growth, and reproduction as well as adversely affecting the essential behaviors of salmon (EPA 2010b). Many watersheds in California's Central Valley, including the San Joaquin and Sacramento Rivers, support several of the salmon addressed in the Biological Opinion (EPA 2010b). The region is also characterized by its extensive agriculture production with over 550,000 lbs of the 12 organophosphates applied in 2009 (CDPR 2010a). Organophosphates are transported off-site to surface waters (SWs) via spray drift, runoff, and irrigation return flows where they may contact salmon and inhibit their acetylcholinesterase, an enzyme that controls chemical signaling by degrading the neurotransmitter acetylcholine (Baldwin et al. 2009).

National Marine Fisheries Service established Reasonable and Prudent Alternatives (RPAs) made up of five elements that the US Environmental Protection Agency (EPA) must implement within 1 year of the final Biological Opinion. The elements outline measures to guarantee that the active ingredients' registrations are not likely to jeopardize the salmon or destroy or negatively alter their critical habitat. One element sets maximum concentration limits (MCLs) for seven organophosphates in salmon habitats that EPA must enforce by using National Marine Fisheries Service' risk reduction measures. MCLs reflect the highest concentrations allowable for salmon habitats, about two times lower than levels at which population growth decline rates occur (EPA 2010b). Two additional MCLs were defined in the Draft Biological Opinion for disulfoton and methyl parathion since their use cancellations were not yet finalized (EPA 2010a). Because National Marine Fisheries Service ranked their risk to salmon as moderate in the Final Biological Opinion, and their use may continue for the next few years, all nine MCLs were included in this analysis.

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The purpose of this analysis was to examine the spatial and temporal trends of the 12 organophosphates and their degradates, specifically the detections exceeding MCLs, from SW monitoring studies conducted in California and compiled by the California Department of Pesticide Regulation (CDPR) from 1991 through 2010. An additional objective was to obtain pesticide use data to determine the correlations between detections and reported applications.

Materials and Methods

The data used to determine the concentrations of the 12 organophosphates—azinphos methyl, bensulide, dimethoate, disulfoton, ethoprop, fenamiphos, methamidophos, methidathion, methyl parathion, naled, phorate, and phosmet—and their degradates in California's SWs were obtained from the CDPR's Surface Water Database (SWD) (CDPR 2010b). SWD contains standardized analytical data from 54 monitoring studies conducted by public and private agencies statewide from 1990 through 2010. SWD contains results from over 330,000 samples collected from rivers, creeks, urban streams, and agricultural drains in 48 counties as well as the San Francisco Bay delta region. They were analyzed for pesticide active ingredients and breakdown products. Any concentration detected above the limit of quantitation (LOQ) of the analytical method was reported as a detection. LOQs were reported for more than 99.5% of the dataset. Data for this analysis was extracted from 46 studies collected from 1991 through 2010 from freshwaters as defined by National Marine Fisheries Service, including intermittent streams, tributaries, drains, ditches, and other manmade conveyances (EPA 2010b). Studies included were spatially and temporally biased and thus not representative of the complete occurrence of organophosphates in California's SWs.

Use data for the organophosphates that exceeded MCLs were acquired from California's Pesticide Use Reporting database, which is also maintained by CDPR. The database compiles comprehensive reports of all agricultural pesticide uses as well as some non-agricultural uses (CDPR 2010a). Urban and residential uses are not reported. Three active ingredients (i.e., bensulide, disulfoton, and phosmet) have registered urban and residential uses in addition to agricultural uses. While disulfoton is under cancellation, bensulide and phosmet have 14 stable, active registrations (CDPR 2010c). Osienski et al.'s (2010) retail survey of outdoor residential pesticides sold in California observed three disulfoton products but no bensulide or phosmet products. Given the limited number of products used in the urban sector, we do not anticipate a significant amount of unreported use to greatly impact the analysis.

MINITAB statistical software (Release 15) was used for all statistical analysis (Minitab Inc. 2007). Data was analyzed using linear regressions relating pesticide use to detections on a month, year, and county basis.

Results and Discussion

There are 47,529 records in the SWD for the 12 organophosphates and 7,065 records for 9 of their degradates (Table 1). The degradate monitoring data were limited to disulfoton sulfone, fenamiphos sulfone, fenamiphos sulfoxide, and the oxygen analogues (OAs) of azinphos methyl, methidathion, methyl parathion, naled, phorate, and phosmet. Methyl parathion was the most frequently sampled (44 studies) and bensulide was the least frequently sampled (1 study) (Table 1). There were 82 different LOQs reported, ranging from 0.001 to 10 µg/L. Over half of the data had an LOQ of 0.05 or 0.1 µg/L. The spatio-temporal distribution of sampling was also variable. The samples analyzed for the 12 organophosphates and 9 degradates were collected from 46 counties from 1991 through 2010; none were collected in 1990 and less than 1% of the samples were collected in 2010. Samples from five counties—Stanislaus, Merced, San Joaquin, Sacramento, and Sutter—made up over two thirds of the total records. Detections from Stanislaus County accounted for more than half of the total detections, followed by San Joaquin County which had 13% of the detections. The samples were collected from 581 sites that included agricultural sloughs, bayous, canals, channels, creeks, culverts, drainage ditches, monitoring stations, rivers, storm drains, urban runoff sites, and wastewater effluents. Pesticides and degradates of interest were detected at over one quarter of the total sites.

Of the 21 organophosphates and degradates analyzed, 12 were detected between 1991 and 2010 (Table 1). Many detections occurred in 1992, 2003, and 2008 with 72–106 detections per year. Bensulide, naled, azinphos methyl OA, fenamiphos sulfone, fenamiphos sulfoxide, methidathion OA, methyl paraoxon, phoratoxon, and phosmet OA were not detected. While dimethoate, disulfoton, ethoprop, and disulfoton sulfone were detected, their concentrations did not exceed MCLs. Azinphos methyl, fenamiphos, and methamidophos were also detected; however, National Marine Fisheries Service did not establish MCLs for them given their registrations are under cancellation (EPA 2010b). No MCLs were established for any of the degradates. Although some of the degradates are more persistent and toxic than their parent compounds and synergistic effects are known to occur when a mixture of organophosphates are present (EPA 2010b), MCLs of the parent compounds were used to compare with their degradates'

Table 1 Detection frequencies and range of detections in comparison to MCLs for salmon habitat (CDPR 2010a, b)

Pesticide	Total records	Detects	Detect freq (%)	Years sampled	Min detect (μg L^{-1})	Max detect (μg L^{-1})	MCL (μg L^{-1})[a]	No. of detects >MCL
Parent compounds								
Azinphos methyl	5,977	26	0.44	91–10	0.006	0.826	–	N/A
Bensulide	20	0	0	04–05, 07	ND[b]	ND	200	0
Dimethoate	5,012	421	8.40	91–10	0.0193	11.31	60	0
Disulfoton	5,562	30	0.54	91–10	0.05	0.22	10	0
Ethoprop	4,179	46	1.10	92–10	0.003	1.11	20	0
Fenamiphos	873	2	0.23	02–10	1.4	1.5	–	N/A
Methamidophos	1,561	3	0.19	06–09	0.24	1.3	–	N/A
Methidathion	6,454	239	3.70	91–10	0.001	15.1	0.3	39
Methyl parathion	7,392	65	0.88	91–10	0.006	1.7	0.1	26
Naled	707	0	0	92–96, 98–02, 04–09	ND	ND	0.2	0
Phorate	5,778	8	0.14	91–10	0.016	0.22	0.1	3
Phosmet	4,014	3	0.07	91–10	0.3	0.63	0.5	1
Degradates								
Azinphos methyl OA[c]	801	0	0	91–95, 05–10	ND	ND	–	N/A
DDVP (dichlorvos)	3,045	2	0.07	91–95, 05–10	0.007	0.242	0.2[d]	1
Disulfoton sulfone	221	19	8.60	05–10	0.01	0.235	10	0
Fenamiphos sulfone	221	0	0	05–10	ND	ND	–	N/A
Fenamiphos sulfoxide	219	0	0	05–10	ND	ND	–	N/A
Methidathion OA	740	0	0	91–95	ND	ND	0.3	0
Methyl paraoxon	801	0	0	91–95, 05–10	ND	ND	0.1	0
Phoratoxon	221	0	0	05–10	ND	ND	0.1	0
Phosmet OA	796	0	0	91–95, 05–10	ND	ND	0.5	0

[a] Established by National Marine Fisheries Service for salmon habitat (EPA 2010a, b)

[b] *ND* no detections

[c] *OA* Oxygen analogue of parent compound

[d] MCL of the parent compound was used for all degradates when available

detections. Methidathion, methyl parathion, phorate, phosmet, and DDVP (the OA of naled) had 70 detections above MCLs, which comprised 22% of the five organophosphates' total detections (Table 1). Methidathion was detected over 50 times higher than the MCL, methyl parathion over 15 times higher, phorate over 2 times higher, and phosmet and DDVP were both about 1.25 times higher.

Analysis of the monthly methidathion and methyl parathion detections reveal seasonal patterns. The highest detection frequencies for methidathion occurred during the rainy season in January and February, while the highest detection frequencies for methyl parathion took place during the irrigation season from May through August (Fig. 1). Accordingly, the majority of methidathion MCL exceedances occurred during January and February, and the bulk of methyl parathion MCL exceedances took place from May through July. All five organophosphates displayed a general growing season use trend. Though, unlike the other organophosphates, the use of methidathion was substantial during January and February in addition to the growing season. The correlation between methyl parathion use and detections was statistically significant ($p < 0.001$) based on regression analysis correlating pounds of pesticide use to detections per month. This linear regression revealed that 81.9% of the methyl parathion detections' variation was accounted for by the monthly methyl parathion use (Fig. 1). While methidathion use did not statistically significantly correlate to increased detections during the rainy season ($p = 0.091$), the monthly use and detections suggest a correlation where peaks in detections and use overlapped. There were not enough phorate, phosmet, or DDVP detections to allow evaluation of seasonal patterns.

The five organophosphates with detections above MCLs displayed yearly detection trends. In general, the highest detection frequencies occurred during the 1990s, apart from DDVP, which was only detected during the last decade. All were monitored extensively over the time period (Table 1). The number of years where there were

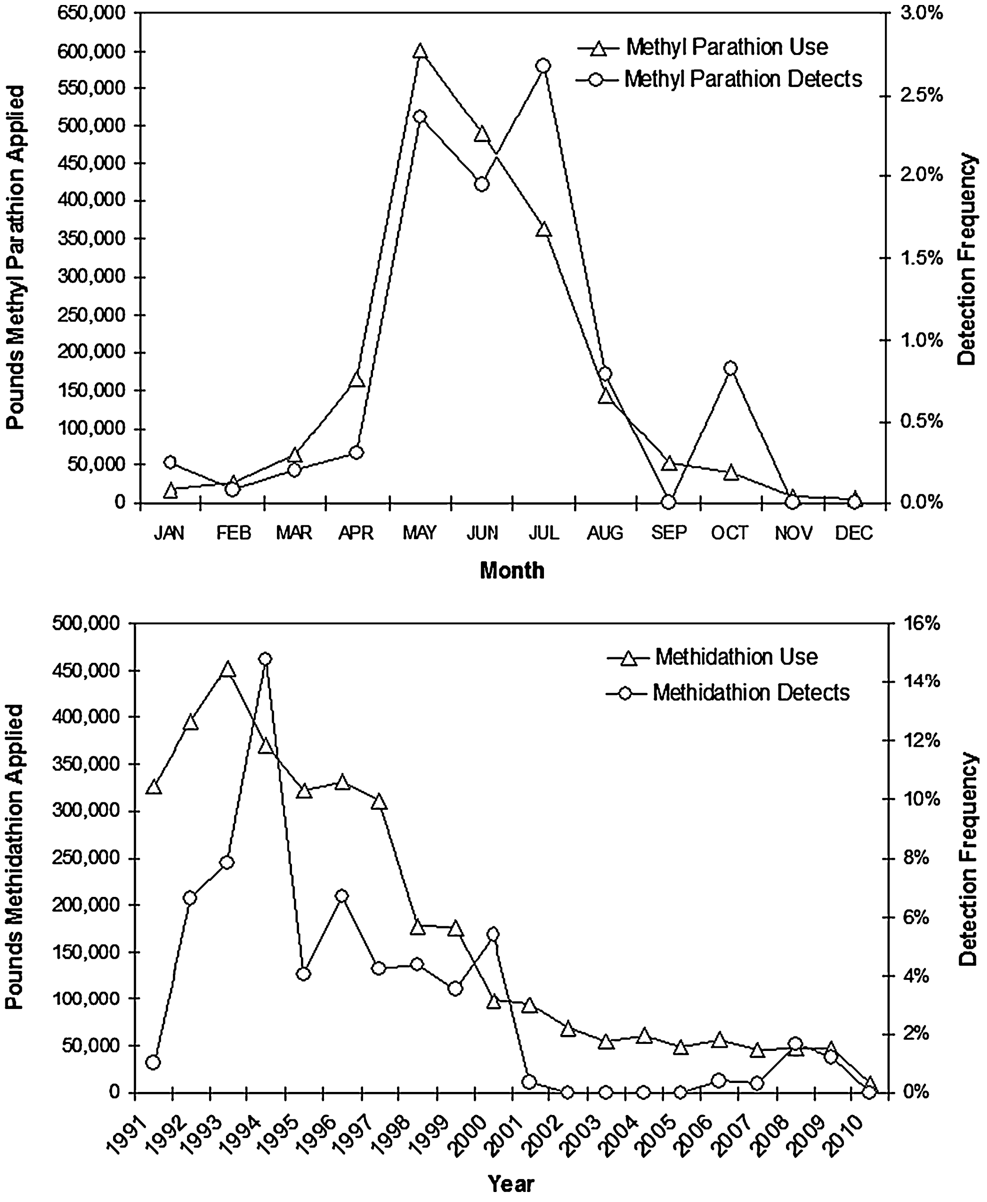

Fig. 1 Methyl parathion and methidathion use and detection trends by month and year, respectively

no detections ranged from 4 to 19 depending on the compound. Similarly, the number of MCL exceedances varied widely from year to year. The majority of methidathion exceedances occurred during 1992, 1993 and 1994; however, exceedances also took place more recently from 2006 to 2008. Methyl parathion exceedances ranged from 1 to 5 per year over a period of 14 years (1995–2008), with the most occurring in 2008. Phorate, phosmet, and DDVP exceedances only occurred during 1 year each. There were no exceedances during 1991, 1999, 2009, or 2010. As a whole, all five organophosphates displayed a general decreasing use trend from 1991 through 2010 (Fig. 1); however, phosmet was applied over two to six times more than the other three parent compounds since 1998. The correlation between methidathion detections to annual use was statistically significant ($p < 0.001$). The use explained 57.6% of the variations in detections (Fig. 1). Methyl parathion detections did not correlate to its use ($p = 0.235$).

Most of the organophosphate detections occurred in waters of the Central Valley (Fig. 2) where 10 of the 28 salmon groups spawn, rear, and migrate (EPA 2010b). The majority of methidathion detections higher than MCLs appeared in San Joaquin (12), Stanislaus (11), and Sutter (6) counties. The bulk of methyl parathion detections exceeding MCLs was sampled from Stanislaus (15), Colusa (4), and Ventura (3) counties. All of the phorate MCL exceedances as well as the one phosmet exceedance were detected in Imperial County. The DDVP exceedance occurred in Stanislaus County. Neither methidathion

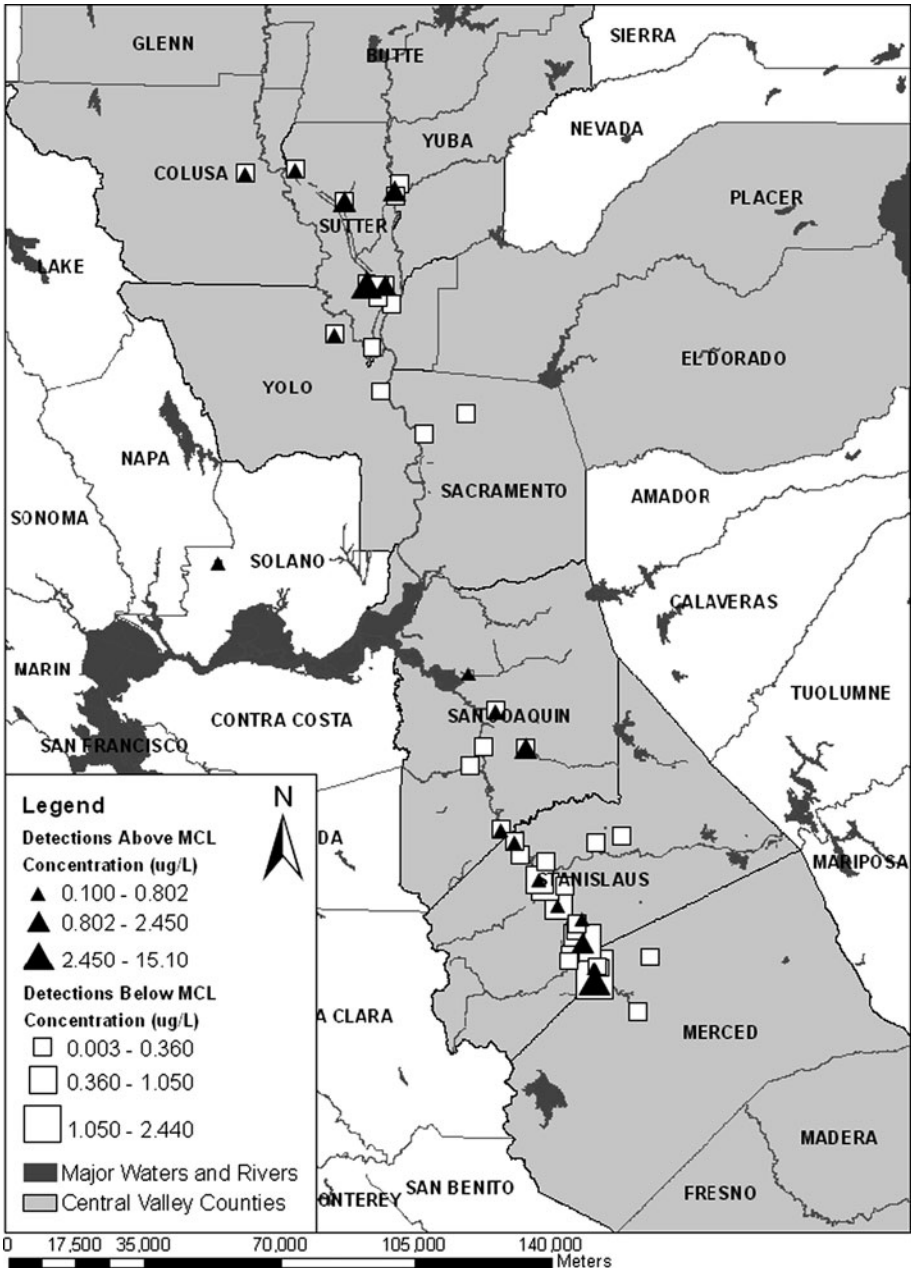

Fig. 2 Geographic distribution of the organophosphates detected above (5) and below (12) maximum concentration limits (MCLs) in California's Central Valley (CDPR 2010a, b)

detections nor methyl parathion detections correlated to use by county, ($p = 0.103$) and ($p = 0.315$), respectively.

Given ample data for methyl parathion and methidathion, their detections may be explained by monthly and yearly use, respectively. Based on the SW detection data evaluated, it is possible that exposures to the five organophosphates exceeding MCLs may continue to jeopardize salmon existence. The extent of exposure may have been underestimated since MCLs did not account for synergism of multiple organophosphates or other stressors. However, the spatial and temporal distribution of sampling does not necessarily coincide with salmon habitats. Still, EPA may have difficulty ensuring that MCLs are not exceeded in the future in California for methidathion, methyl parathion, phorate, phosmet, and naled (given its degradation to DDVP) while the active ingredients are in use and without proper implementation of additional risk reduction measures.

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