Temporal Patterns and Sources of Atmospherically Deposited Pesticides in Alpine Lakes of the Sierra Nevada, California, USA

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Brief: Pesticide concentrations in California alpine lakes track pesticide application rates at agricultural sites over 65 km away.

Abstract

Agricultural pesticides are being transported by air large distances to remote mountain areas, and have been implicated as a cause for recent population declines of several amphibian species in such locations. Largely unmeasured, however, are the magnitude and temporal variation of pesticide concentrations in these areas, and the relationship between pesticide use and pesticide appearance in the montane environment. We addressed these topics in the southern Sierra Nevada mountains, California, by sampling water weekly or monthly from four alpine lakes from mid-June to mid-October 2003. The lakes were 46-83 km from the nearest pesticide sources in the intensively cultivated San Joaquin Valley. Four of 41 target pesticide analytes were evaluated for temporal patterns: endosulfan, propargite, dacthal, and simazine. Concentrations were

very low, approximately 1 ng/L or less, at all times. The temporal patterns in concentrations differed among the four pesticides, whereas the temporal pattern for each pesticide was similar among the four lakes. For the two pesticides applied abundantly in the San Joaquin Valley during the sampling period, endosulfan and propargite, temporal variation in concentrations corresponded strikingly with application rates in the Valley with lag times of 1-2 weeks. A finer-scale analysis suggests that a large fraction of these two pesticides reaching the lakes originated in nearby upwind areas within the Valley.

Introduction

The Sierra Nevada mountains of California lie downwind from one of the most intensively cultivated areas in the United States, the Central Valley of California. Consequently, ecosystems throughout the mountains, including those in national parks and wilderness areas, have been exposed to airborne pesticides and other pollutants [1]. Pesticides from presumed regional sources have been documented in multiple physical and biotic media, including areas up to 3500 m elevation and many tens of kilometers from the nearest sources in the Central Valley [2-9]. Although measured pesticide levels have generally been well below various acute toxicity levels, p,p'-DDE concentrations in fish in two alpine lakes in the southern Sierra recently exceeded a health threshold for kingfishers [7]. There is also concern for ecological effects because most measurements have been made only once and thus do not capture temporal variation, an important consideration for a region where pesticides are applied year round and their use varies tremendously in time and space. Moreover, organisms in the Sierra are exposed to complex mixtures of pesticides, which may have greater effects than exposure to individual pesticides [3, 10], and some of these compounds may interact with other stressors such as disease [11].

Of particular concern in the Sierra Nevada/Cascades region of California has been the disappearance in recent decades of numerous populations of at least seven species of native amphibians with few observed changes in habitat or other factors [12-14], although some disease impacts have been documented recently [15]. Most conspicuous of these declines has been the mountain yellow-legged frog complex (*Rana muscosa* complex, recently split into *R. muscosa* and *R. sierrae*; [14]), a taxon formerly the most ubiquitous aquatic vertebrate in lakes and streams at higher elevations in the Sierra Nevada [16]. Atmospherically deposited pesticides have been implicated as a cause for these declines, acting by themselves or in concert with other factors such as fish introductions and disease [5, 17-19]. However, measurements for pesticides in the alpine waters commonly inhabited by these species have been taken in recent decades from only a few locations [5, 6, 8], and almost no data are available for temporal variation in pesticide levels.

The present study was designed to measure pesticide levels at trace (ng/L) or ultatrace (pg/L) levels over time at several sites in the aquatic habitat of *R. muscosa* and *R. sierrae* to characterize the magnitude and temporal variation in pesticide levels. We also evaluated temporal variation of pesticide concentrations as a function of pesticide application in specific areas to identify potential source locations. We focused on high elevation lakes in the southern Sierra Nevada because these two frog species have been extensively studied here [5, 13-15, 19], and the region is located adjacent to the San

Joaquin Valley, the southern arm of the Central Valley where pesticide use is greatest (based on California Department of Pesticide Regulation annual pesticide use reports, http://calpip.cdpr.ca.gov).

Experimental Section

We selected four high-elevation lakes in Sequoia and Kings Canyon National Parks, California: two relatively near the San Joaquin Valley (46-55 km) and two far from the Valley (68-83 km) between 27 and 45 km apart (See Supporting Information for details of site selection and Table S1 and Fig. S1 for location and characteristics of lakes). Water samples were collected weekly at the lake nearest the San Joaquin Valley (Frog Lake), and at 4-week intervals at the other three lakes (Gorge, East Marjorie, and Wright lakes), from mid-June to mid-October 2003. These lakes varied in elevation (3042–3645 m), area (1.3–17.2 ha), maximum depth (3.5–15.1 m), and watershed area (53-197 ha). Water temperature was low (e.g., $< 7^{o}$ C) during sampling in lakes that were still largely ice-covered on the first sampling date in June (Frog, Wright, and East Marjorie lakes), and averaged between 12.3 and 16.1^{o} C among the lakes overall. Throughout the sampling period at all lakes, pH was circumneutral and specific conductance was very low. Dissolved oxygen, measured only at Frog Lake, was >85% saturation at all depths throughout the sampling period. Rainfall from local thunderstorms, measured with plastic rain gages near ground level, fell during five weekly intervals at Frog Lake and two of the corresponding monthly intervals at the other three lakes.

Precipitation in the study area occurs mainly as snow during the winter months of November through March. Precipitation during these months in 2002-2003 was 89% of the 30-year average at Lodgepole, 8 km west of Frog Lake. We evaluated air flow pathways to Frog Lake by modeling 24-hour back-trajectories every three hours between 0600 and 1800 hours PDT from a point on the edge of the San Joaquin Valley that comprises the approximate origin for upslope winds to Frog Lake (see Supporting Information for details). Tracer and meteorological studies show that during a typical summer day surface air from the southeast side of the Valley is transported into the southern Sierra Nevada by diurnal upslope flows, reaching the Frog Lake area by midafternoon [1, 20, 21]. Pesticide application data came from pesticide use reports of the California Department of Pesticide Regulation (http://calpip.cdpr.ca.gov). None of the pesticides detected in the study was applied in the mountains during 2003.

Water samples (100 L) were extracted in the field using an on-line filtration/extraction assembly that consisted of a battery-powered ceramic pump, Teflon tubing, glass fiber filter, and a solid phase extraction (SPE) cartridge (see Supporting Information for details of sampling apparatus). Abselut Nexus (Varian Inc., Harbor City, CA) was used as solid phase sorbent. Forty-one compounds (i.e., pesticides and some of their degradation products) were extracted and analyzed using methods developed and optimized for 100-L water samples [22]., except that a less stringent method was used in the present study to calculate estimated method detection limits (MDL; see Supporting Information for MDL calculation method and Table S2 for recoveries and MDL values). The less-stringent calculation method was used to increase the potential to detect a temporal pattern in concentrations and to be more consistent with previous analyses in alpine lake water in the study region [3]. A total of 35 samples (including 4 duplicate pairs) and 5 field blanks were collected (see Supporting Information for details).

For statistical analysis, concentration values < MDL were replaced with 1/2 of the MDL. Values for duplicate samples were averaged. Time dependency of pesticide concentrations between sequential weekly samples at Frog Lake was evaluated by autocorrelation (correlogram) analysis [23]. Association between the temporal pattern of pesticide concentrations in Frog Lake and pesticide applications in the San Joaquin Valley was evaluated by cross-correlation (cross-correlogram) analysis [23]. This analysis computes a correlation coefficient between the two variables (i.e., pesticide concentration and weekly application rate) at different lag times (i.e., 0 week, 1 week, 2 weeks, etc.). We evaluated this association at two scales: the entire valley and individual townships, which are approximately 10 km on side. Cross-correlation analysis was also used to evaluate association between temporal patterns among the individual pesticides in Frog Lake.

We used ANOVA to evaluate differences in pesticide concentrations among lakes. Concordance of temporal patterns in pesticide concentrations among the four lakes was evaluated by comparing the coincidence of the four inter-sample trend directions for each chemical (i.e., peaks and valleys occurring at the same times). The probability that at least three of the four lakes would have the same configuration of peaks and valleys by chance is 0.0148 (see Supporting Information for calculation details). We used SAS v. 9.1 (SAS Institute Inc., Cary, NC) for statistical analyses and Surfer 8 (Golden Software, Inc., Golden, CO) for kriging distributions of pesticide application.

Results and Discussion

Pesticides Found. Eight of the 41 pesticide analytes were detected at least once among the four lakes (see Supporting Information, Table S3). Four of the eight were found frequently, allowing us to evaluate temporal patterns: endosulfan I (an insecticide and acaricide), propargite (an acaricide), and dacthal and simazine (herbicides). Endosulfan II was also found in a number of samples, but less frequently and usually in much lower concentrations than endosulfan I; the two forms were combined for analysis. Concentrations of these pesticides were very low in all four lakes, generally less than 1 ng/L for endosulfan I+II, propargite, and dacthal, and only slightly higher for simazine (Figs. 1 and 2). Endosulfan I or II, dacthal, and simazine were detected in all four lakes, whereas propargite was detected only in Frog Lake (Fig. 2 and Supporting Information Fig. S2). Concentrations for three less frequently detected pesticides, chlorothalonil, trifluralin, and chlorpyrifos, were also very low (< 0.07 ng/L in all cases; see Supporting Information, Table S3).

These findings are consistent with concentrations for the few other lake-water samples from the vicinity, as well as for snowpack samples. Within 4 km of Frog Lake, similar concentrations were found for endosulfan in two lakes in 1997 [5], for endosulfan and dacthal in two other lakes in 2003 [8], and for endosulfan and dacthal in the cumulative snowpack [6]. Relatively low concentrations for endosulfan and dacthal have also been found in other media in the vicinity in 2003 or 2005, including air (B-endosulfan , ~10 pg/m^3), sediment, vegetation, fish, and tadpoles [8, 9].

As discussed below, it appears unlikely that concentrations for the four recurring pesticides would have been substantially greater at other times of the year than our observed levels. The maximum concentrations observed for the four pesticides were three to eight orders of magnitude lower than benchmarks for effects on aquatic life, except for endosulfan, which was lower by a factor of 37 [24, 25]. Among the four pesticides, toxicity data for amphibians are available only for endosulfan. The maximum concentration of endosulfan observed in the present study (~ 1 ng/L) was lower than the lowest-observed-effect concentration among nine anuran tadpoles exposed for 8 d (2000 to 60,000 ng/L [26]), the concentration inducing sublethal effects in *Bufo bufo* tadpoles after 43 d (10,000 ng/L [27]), and the 96-h LC_{50} for tadpoles of *Rana boylii* (550 ng/L [28]) and *Hypsiboas pulchellus* (130 ng/L [29]).

Temporal Patterns of Pesticide Concentrations. The temporal patterns of concentrations for the four pesticides were largely independent of each other. For Frog Lake, concentrations at weekly intervals were not significantly related to each other (cross-correlation analysis for pairwise combinations of pesticides; Fig. 1). Endosulfan showed a sharp peak in concentration in mid-September, propargite showed a sharp peak in late July, dacthal showed a variable plateau from late July to early October, and simazine showed multiple peaks. Such apparent independence in temporal patterns among pesticides was also evident for monthly sampling for the three pesticides represented at all four lakes. Specifically, endosulfan showed a peak in September or October, dacthal showed a valley in July and a peak in September or October, and simazine showed a valley in July, August, or September (Fig. 2 A, C, and D).

Sampling at 1-week frequency in Frog Lake generally captured the temporal variation of three of the four pesticides (endosulfan I+II, propargite, and dacthal; Fig. 1A, B, and C). That is, autocorrelation analysis indicated that samples one week apart were significantly correlated with each other ($p < 0.05$), indicating that the value at a given time was partially dependent on the value for the previous week. For simazine, however, there was no significant time dependency among samples, although it appears that this lack of significance can be attributed largely to the highly variable concentrations during the first half of the sampling period (Fig. 1D).

Consistency of Temporal Patterns Among Lakes. The four lakes showed similar temporal patterns for the three pesticides that were found in all four lakes (i.e., endosulfan, dacthal, and simazine; Fig. 2A, C, and D). For endosulfan and dacthal, trend reversals (i.e., peaks and valleys) occurred at identical times for three of the four lakes for each chemical (i.e., Frog, E. Marjorie, and Gorge lakes). The probability of this or more extreme concordance occurring by chance was 0.0148 for each chemical. Thus, the processes that determine the temporal patterns of individual pesticides appear to be very similar among lakes. The temporal patterns in Wright Lake, however, differed somewhat from the other three lakes (Fig. 2A, C, and D). These differences may be because Wright Lake is in the Kern watershed, which contrasts from the other two watersheds in the study (Kaweah and Kings) by having a north-south orientation rather than an east-west one (see Supporting Information, Fig. S1). Air within the upper Kern watershed during summer is thought to consist largely of air moving upslope/downslope within the watershed and air mixed in from the Kaweah watershed along the ridgeline separating the two watersheds [20].

Differences in Pesticide Concentrations Among Lakes. The four lakes differed from one another in pesticide concentrations in a consistent manner throughout the study. Frog Lake invariably had the highest concentration for each sampling time for three of the four pesticides (endosulfan I+II, propargite, and simazine) during those times when the pesticide was detected at any lake. This finding is evident in Fig. 2, but a better comparison among the lakes is achieved by normalizing the concentrations relative to the maximum concentrations among the four lakes for each sampling time (see Supporting Information Fig. S3). The resultant relative concentrations for the above three pesticides were significantly higher in Frog Lake than in the other three lakes (ANOVA, $p < 0.005$ for each of the three pesticides), whereas the values in the other three lakes were not significantly different from each other. Relative concentrations for the fourth pesticide, dacthal, did not differ significantly among the lakes.

These differences among lakes were not obviously related to lake characteristics such as lake depth, lake surface area/volume ratio, watershed area, drainage orientation or other factors (See Supporting Information, Table S1). These differences were apparently also not related to time of spring overturn, which occurred around the time of the first monthly sampling in Frog, East Marjorie, and Wright Lakes, but occurred prior to first sampling in Gorge Lake. Cold condensation processes were also apparently not involved in determining concentration differences among lakes because elevation showed no relationship to concentration (see Supporting Information, Table S1) However, the finding that the lake closest to the San Joaquin Valley (Frog Lake) had the highest concentrations (Fig. 2 and Supporting Information Fig. S3) is consistent with the prediction that contaminant exposure decreases with distance from the Valley [5, 19].

Inconsistent with this prediction, though, was that Gorge Lake (the second closest lake to the Valley) was significantly lower in pesticide concentrations than Frog Lake and not significantly different from either of the two more distant lakes. Moreover, Bradford et al. [9] did not find a consistent association with distance for pesticides in air, sediment, or tadpoles among high-elevation sites in the southern Sierra Nevada.

Source Locations for Endosulfan and Propargite. Tens to hundreds of metric tonnes of endosulfan and propargite were applied to crops in the San Joaquin Valley during the sampling period (See Supporting Information, Fig. S4). Application rates (kg/wk) varied during this period, and corresponded with temporal variation in concentrations in Frog Lake. For endosulfan (Fig. 1A), the highest significant cross-correlation coefficient (0.780) was for lag 1 (i.e., concentration in Frog Lake lagged application by one week). This lag is most evident by comparing the peak in application rate in early September with the peak in concentration in lake water a week later. For propargite (Fig. 1B), the match between the temporal patterns for application rate and concentration in lake water was more striking, with the highest significant cross-correlation coefficient (0.841) occurring at lag 2 (i.e., concentration in Frog Lake lagged application by two weeks).

While it is possible that such concordance resulted from mixing of pesticides in air from throughout the San Joaquin Valley, it is also possible that the pesticides reaching Frog Lake came predominantly from subareas within the Valley. If we assume the latter and that the source subareas encompass multiple townships, then we would expect high cross-correlation coefficients between concentrations in Frog Lake and pesticide application rates for the townships within such clusters. For both endosulfan and propargite, cross-correlation analysis at the township scale showed significant correlations for many townships in the San Joaquin Valley (Fig. 3A and B). For both pesticides, the largest cluster of adjacent townships with high correlation coefficients was relatively close to Frog Lake within the Valley. For endosulfan (Fig. 3A), the center of this cluster of 6 townships was about 20 km west-northwest of the approximate origin for diurnal upslope winds to Frog Lake (and 68 km from Frog Lake); for propargite (Fig. 3B), the approximate center of the cluster of 15 townships was about 70 km northwest of this point (and 105 km from Frog Lake; see Fig. 1A and B legend for application rates for these township clusters). Interestingly, endosulfan application was low within the cluster relative to elsewhere in the valley, as indicated by contour lines in Fig. 3A.

Back-trajectory analysis from the approximate origin for diurnal upslope winds to Frog Lake (Fig. 3C) showed predominantly northwest air flows, a direction expected for the season [30, 31]. Typically, the 24-hour back trajectories originated in the northern end of the San Joaquin Valley, and frequently passed through the clusters of townships identified above for endosulfan and propargite. Thus, it is plausible that a large fraction of these two pesticides in Frog Lake originated within these clusters. The difference in location of the two clusters may be because only small amounts of endosulfan were applied northwest of the township cluster for endosulfan (as indicated by contours in Fig. 3A), whereas propargite application in this portion of the Valley was widespread (Fig. 3B).

The temporal patterns for endosulfan and propargite concentrations in lake water throughout the year are likely driven primarily by the application of these pesticides at upwind agricultural sites in the San Joaquin Valley. For endosulfan, winter and spring application showed a low peak during February-March (see Supporting Information, Fig. S4), and an average of 1.4 ng/L total endosulfan (i.e., endosulfan I, II, and sulfate) was found in the cumulative snowpack around April 1, 2003 at two sites 2.8 and 3.7 km SW of Frog Lake [6]. Thus, some endosulfan likely entered Frog Lake and the other lakes during the primary snowmelt period (April through June). However, no endosulfan I or II was detected in any lake during the latter portion of this period (i.e., mid-June; Figs. 1A and 2A). Subsequently, endosulfan appeared in Frog Lake and the levels were significantly correlated with application rates in the San Joaquin Valley. For propargite, winter application was virtually none (see Supporting Information, Fig. S4), and it was not detected in Frog Lake in June or early July. Subsequently, however, it appeared in Frog Lake and its levels closely tracked application rates in the San Joaquin Valley. The low concentrations observed for propargite, relative to its high application rates (Figure 1) are likely at least partly due to strong soil and sediment adsorption. Propargite has the highest K_{oc} and K_{ow} of the four pesticides [32] .

Source Locations for Dacthal and Simazine. In contrast to endosulfan and propargite, application of dacthal and simazine was very low in the San Joaquin Valley during the sampling period; however, dacthal was applied abundantly in the central coastal region of California (See Supporting Information, Fig. S4). Cross-correlation analyses between the concentrations in Frog Lake and application rates in the San Joaquin Valley or coastal California were not significant for these two pesticides, and there was no suggestion that peaks of concentration in Frog Lake followed peaks in application (Fig. 1C and D).

Thus, the source locations and factors determining the temporal pattern of concentrations for dacthal and simazine in the lakes are not clear. Hageman et al. [6] predicted that nearly 100% of the dacthal in the snowpack in the vicinity of our study lakes comes from regional sources. Winter storms in the Sierra typically pass across the central coast, where dacthal is applied abundantly year round, and the San Joaquin Valley, where simazine is applied abundantly in winter (See Supporting Information, Fig. S4). Hageman et al. [6] reported dacthal concentrations averaging 4.6 ng/L in the snowpack at the end of the snow accumulation period in 2003 at two high-elevation sites approximately 3 km southwest of Frog Lake. A large fraction of dacthal in the snowpack would likely enter the lakes through snowmelt water [33], and the same outcome could be expected for simazine because it is relatively polar like dacthal. Indeed, dacthal and simazine were present in 3-4 lakes during the first week of the study when snowmelt runoff was still pronounced. Thereafter, the temporal patterns of concentrations in the lakes may reflect atmospheric inputs from areas sprayed months previously, persistence of the pesticides in the lake ecosystems, or complex pathways for airborne transport from source to lake.

Mechanism of Pesticide Deposition. The concordance between the temporal patterns of application rates and concentrations of endosulfan and propargite in Frog Lake strongly suggests that at least these two pesticides were transported by air during the study period and deposited on the lake or its watershed. However, it is not possible to determine the relative contributions of dry deposition to the lake surface, wet deposition to the lake surface, and rainfall washing dry-deposited material into the lake. Dry deposition to the lake surface is presumably involved because the concentration patterns in lake water for endosulfan and propargite generally followed the application rates pattern regardless of rainfall events (Fig. 1A and B). Nevertheless, input via rainfall is suggested by the initial peaks in endosulfan and dacthal in Frog Lake on July 24 that coincided with the onset of a period of rainfall (Fig. 1A and C). During the previous week, which lacked rainfall, concentrations changed very little.

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Supporting Information Available

Details of methods are provided for site selection, water sampling, extraction and analysis of pesticides, environmental measurements, calculation of probabilities for coincidence of pesticide temporal pattern among lakes, and calculation of air flow back trajectories. Also provided are tables for characteristics of study sites, target analytes and their method detection limits, and sample results, and figures showing site locations, frequency of pesticide occurrence in each lake, relative concentrations of each pesticide among the four lakes, and pesticide amounts applied by month throughout California.

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Figure Legends

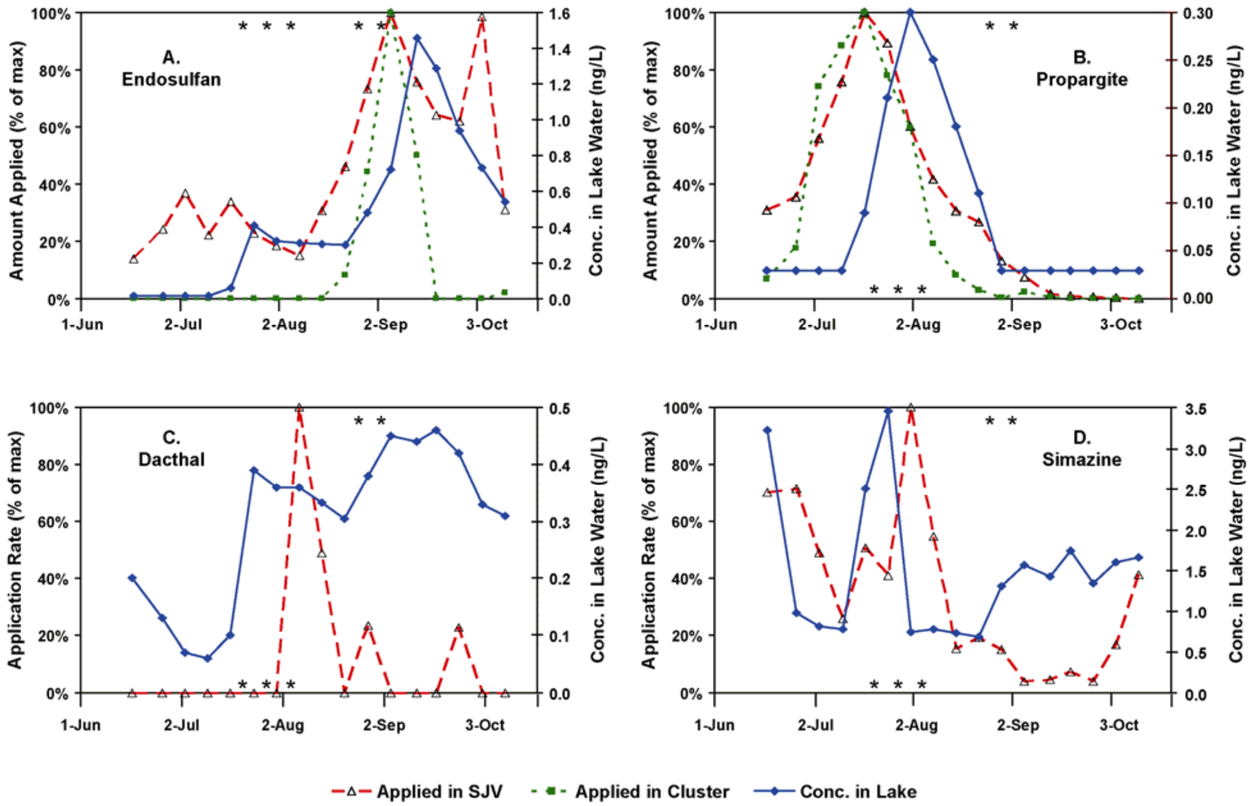
Figure 1. Concentrations of pesticides in Frog Lake, sampled weekly from June 17 to October 9, 2003 (solid blue line), and corresponding weekly pesticide application rates in the San Joaquin Valley. Non-detection of a pesticide is shown as ½ of MDL (0.017 ng/L for endosulfan I+II and 0.029 ng/L for propargite). The concentrations in Frog Lake on August 14 were interpolated. Application rate for each date is the amount of active ingredient applied during the previous 7 days, expressed as a percentage of the maximum 7-day rate during the study period. Application is represented for the entire San Joaquin Valley (SJV; red long-dashed line) and for the largest cluster of adjacent townships with high cross-correlation coefficients in the analysis for concordance of temporal patterns (green short-dashed line; endosulfan and propargite only). Asterisks indicate five inter-sample intervals when rainfall occurred at Frog Lake (4.06, 3.30, 0.94, 1.40, and 0.64 cm, in chronological order). A. Endosulfan. Maximum application rate was 4698 kg/wk for the San Joaquin Valley and 695 kg/wk for the cluster of 6 adjacent townships with high cross-correlation coefficients southwest of Frog Lake (Fig. 3A). B. Propargite. Maximum application rate was 65,030 kg/week for the San Joaquin Valley and 6888 kg/wk for the cluster of 15 adjacent townships with high cross-correlation coefficients west of Frog Lake (Fig. 3B). C. Dacthal. Maximum application rate for the San Joaquin Valley was 215 kg/week. D. Simazine. Maximum application rate for the San Joaquin Valley was 713 kg/week.

Figure 2. Concentrations of four pesticides in surface water of the four lakes, sampled at 4-week intervals from mid-June to mid-October 2003. Values for Frog Lake

on August 14 were interpolated from values measured 7 days before and after this date. Non-detection of a pesticide is shown as 1/2 of MDL (as in Fig. 1 for endosulfan and propargite; 0.021 ng/L for simazine). Computation of P-values is described in text. Measurable rainfall occurred at all four lakes during the intervals ending on the August and September sampling dates.

Figure 3. Comparison between the temporal patterns of pesticide application in individual townships in the San Joaquin Valley and pesticide concentrations in Frog Lake (star), and air flow back-trajectories. A. Endosulfan. Gray cells indicate townships with any endosulfan application during the period June 11 – October 9, 2003. Red cells indicate townships with high and significant cross-correlation coefficients (i.e., $r > 0.6$) for the comparison of lake concentration to application rate within the township. Blue contour lines indicate pesticide loading in 3 kg/km^2 increments for the above time period derived by kriging loading values for the centroid of each township. Heavy line indicates approximate boundary between mountainous terrain and San Joaquin Valley. Dark polygons indicate Sequoia and Kings Canyon National Parks, and light green lines indicate county boundaries. Arrow indicates approximate pathway of diurnal upslope winds during summer from valley edge to Frog Lake area [20, 21]. B. Propargite. Features same as in A, except contour increments are 8 kg/km^2, and green cells indicate townships with cross-correlation coefficients >0.75. C. Twenty-four hour back-trajectories starting at the approximate origin for upslope winds to Frog Lake. Each dot is the hourly location of a back-trajectory. The largest cluster of adjacent townships with high cross-correlation coefficients for endosulfan and propargite, identified from A and B above, are indicated. Other features as in A.

Figure 1



A.
Endosulfan
B.
Propargite
C.
Dacthal
D.
Simazine
Amount Applied (% of max)
Application Rate (% of max)
Conc. in Lake Water (ng/L)
100%
80%
60%
40%
20%
0%
1-Jun
2-Jul
2-Aug
2-Sep
3-Oct
Applied in SJV
Applied in Cluster
Conc. in Lake

Figure 2

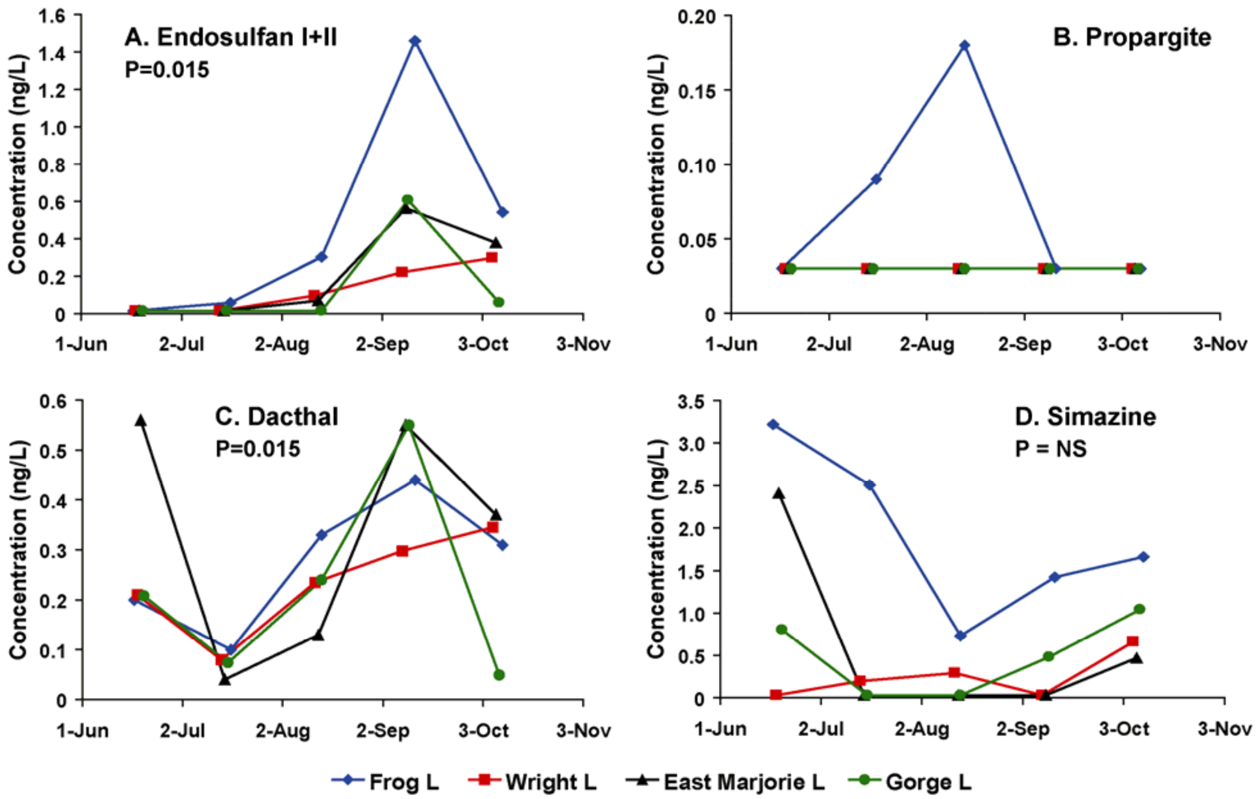
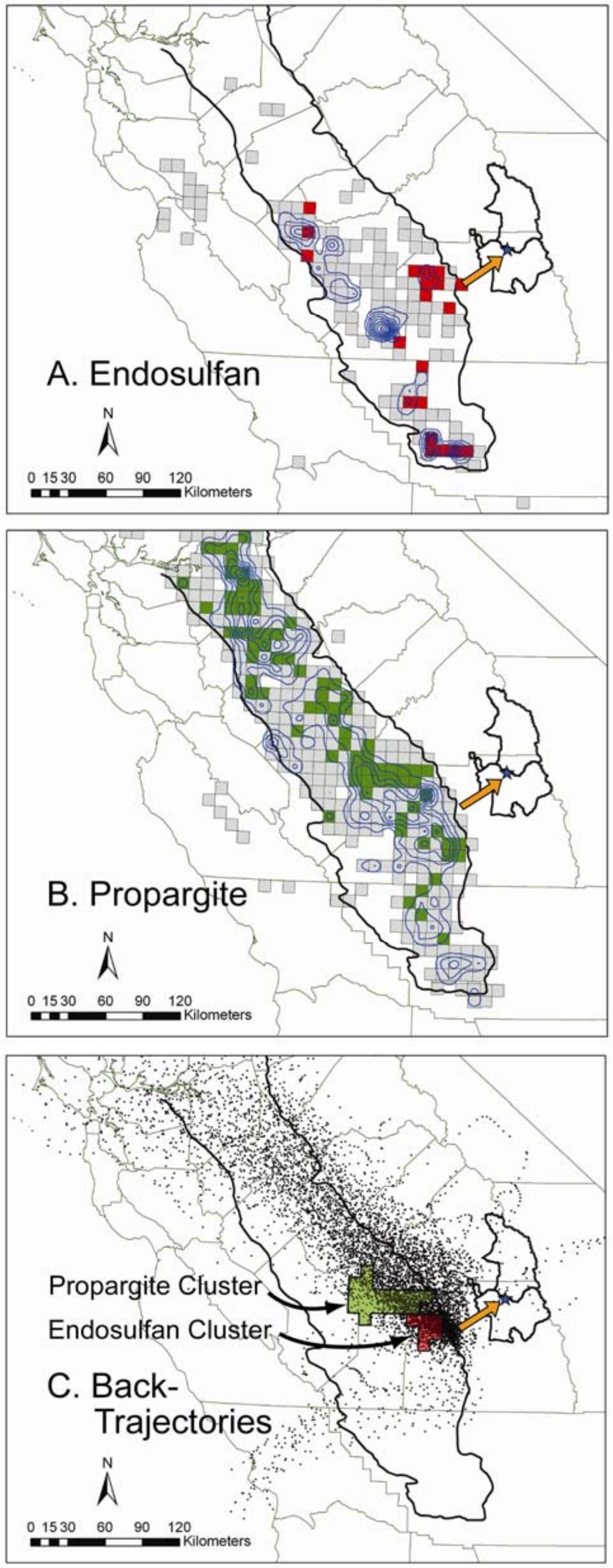

A. Endosulfan I+II
P=0.015
B. Propargite
C. Dacthal
P=0.015
D. Simazine
P = NS
Concentration (ng/L)
1-Jun
2-Jul
2-Aug
2-Sep
3-Oct
3-Nov
Frog L
Wright L
East Marjorie L
Gorge L

Figure 3


A. Endosulfan
N
0 15 30 60 90 120
Kilometers
B. Propargite
N
0 15 30 60 90 120
Kilometers
Propargite Cluster
Endosulfan Cluster
C. Back-
Trajectories
N
0 15 30 60 90 120
Kilometers