Published in final edited form as:

Environ Toxicol Chem. 2010 May ; 29(5): 1056–1066. doi:10.1002/etc.139.

Spatial Patterns of Atmospherically Deposited Organic Contaminants at High-Elevation in the Southern Sierra Nevada Mountains, California, USA

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Abstract

Atmospherically deposited contaminants in the Sierra Nevada mountains of California, USA have been implicated as adversely affecting amphibians and fish, yet little is known about the distributions of contaminants within the mountains, particularly at high elevation. We tested the hypothesis that contaminant concentrations in a high-elevation portion of the Sierra Nevada decrease with distance from the adjacent San Joaquin Valley. We sampled air, sediment, and tadpoles twice at 28 water bodies in 14 dispersed areas in Sequoia and Kings Canyon National Parks (2785 – 3375 m elevation; 43 – 82 km from Valley edge). We detected up to 15 chemicals frequently in sediment and tadpoles, including current- and historic-use pesticides, polychlorinated biphenyls, and polycyclic aromatic hydrocarbons. Only β -endosulfan was found frequently in air. Concentrations of all chemicals detected were very low, averaging in the parts-per-billion range or less in sediment and tadpoles, and on the order of 10 pg/m³ for β -endosulfan in air. Principal components analysis indicated that chemical compositions were generally similar among sites, suggesting that chemical transport patterns were likewise similar among sites. In contrast, transport processes did not appear to strongly influence concentration differences among sites because variation in concentrations among nearby sites was high relative to sites far from each other. Moreover, a general relationship for concentrations as a function of distance from the valley was not evident across chemical, medium, and time. Nevertheless, concentrations for some chemical/medium/time combinations showed significant negative relationships with metrics for distance from the Valley. However, the magnitude of these distance effects among high-elevation sites was small relative to differences found in other studies between the valley edge and the nearest high-elevation sites.

Keywords

Amphibian; Polycyclic aromatic hydrocarbon; Polychlorinated biphenyl; Pesticide; Tadpole

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INTRODUCTION

The Sierra Nevada mountain range lies adjacent to one of the highest pesticide-use areas in North America, the Central Valley of California [1]. The occurrence of pesticides and other airborne contaminants in the mountains has been well documented over several decades (e.g., [1,2,3–12]), and evidence has been provided that the primary source of both current- and historic-use pesticides in the Sierra is the adjacent valley (e.g., [5,12]). Recently, airborne pesticides have been implicated as a causal factor in the dramatic population declines of several frog species in the Sierra Nevada region [6,9,13–16]. Moreover, concentrations for dichlorodiphenyltrichloroethane (DDT)-related compounds and dieldrin in some fish collected recently at high elevation sites in Sequoia National Park exceeded human health thresholds for recreational fishing and/or wildlife health thresholds [11].

Despite the implication of contaminants in causing adverse effects, little is known concerning contaminant distributions within the mountains, particularly at high elevation. Consequently, resource managers have little knowledge for the magnitude and variation in chemical concentrations and little insight for where contaminant effects are most likely to occur. Many mountain ranges, including the Sierra Nevada, can act as regional convergence zones for some organic chemicals as a result of diurnal mountain winds and increased precipitation and lower temperatures in comparison to surrounding terrain [17]. Thus, concentrations within mountains may not be monotonically related to distance from a source and, for some chemicals, concentrations may increase with elevation. For example, organophosphate pesticides generally decrease along distance/elevation gradients, whereas more persistent chemicals such as DDT-related compounds, endosulfan, and polychlorinated biphenyls (PCBs), have been shown to increase with elevation in some cases [17,18]. Separating the influence of distance from elevation, however, can be difficult because the two factors are often correlated in gradient studies, i.e., elevation increases as distance from a source increases [17]. In the southern Sierra Nevada, though, the alpine zone extends to over 30-km wide and offers an opportunity to evaluate the influence of distance on contaminant concentrations while holding elevation more-or-less constant.

Several studies in the Sierra Nevada mountain range have examined concentrations of airborne pesticides in various media along distance/elevation gradients from the adjacent San Joaquin Valley (i.e., southern arm of the Central Valley; [1,2,5,7,8,10]). In general, concentrations of pesticides and PCBs decreased along these gradients, although relatively few sites were represented from high elevation (i.e., >2800). However, limited data from three studies [8–10] also suggest a decrease in pesticide and PCB concentrations with distance from the Valley even within the high-elevation zone. Davidson and Knapp [14] provide a predictive framework for evaluating pesticide distributions in the southern Sierra Nevada mountain range by showing that a metric for extent of upwind pesticide use decreases monotonically with distance from the Valley.

To better understand distribution patterns for chemical contaminants in the mountains, the present study tested the hypothesis that concentrations of atmospherically deposited chemicals at high elevation in the southern Sierra Nevada mountain range decrease with distance from the San Joaquin Valley. The goal of the present study was to evaluate the generality of resulting patterns with distance across many chemicals (including both current- and historic-use pesticides), three media (air, sediment, and tadpoles), and two sampling periods. The influence of tadpole developmental stage on chemical concentrations in tissue was also evaluated and included in the analyses for distance relationships.

The study focused on water bodies at high elevation (>2750 m) because they are abundant and comprise habitat for the frogs and fish implicated as adversely affected by pesticide exposure in the mountains [11,14]. The study was conducted in the southern Sierra Nevada primarily because airborne contaminant concentrations are generally greater at the southern end of the Sierra Nevada than further north [3,6,19], pesticide use in the adjacent San Joaquin Valley greatly exceeds that in the Sacramento Valley to the north (California Department of Pesticide Regulation Pesticide-Use Reports; <http://www.cdpr.ca.gov/docs/pur/purmain.htm>), and water bodies at similar elevations vary in distance from the San Joaquin Valley by over two-fold. To evaluate the magnitude of our observed distance-concentration relationships at high elevation relative to the magnitude of variation over the entire distance/elevation gradient from the Valley to the crest of the mountain range, we compared results of the present study from high elevation with those from other studies conducted nearer the Valley.

MATERIALS AND METHODS

Study area and site selection

The study area encompassed the high-elevation portions (> 2750 m) of the three major watersheds in Sequoia and Kings Canyon National Parks (i.e., Kings, Kaweah, and Kern Rivers). We selected fourteen areas dispersed throughout the three watersheds, representing distances relatively near and far from the San Joaquin Valley, that contained abundant populations of *Pseudacris regilla* (Pacific treefrog; Fig. 1). Within each area two water bodies (i.e., sites) were selected in which *P. regilla* was common, one with a depth of at least 1 m, and the other at least 200 m away and of any depth (distance apart averaged 0.8 km; range 0.2 – 2.8 km). *Pseudacris regilla* was selected for sampling because it is widespread and abundant throughout the study area. Fish were absent from all water bodies or the isolated portions of the water bodies where tadpoles and sediment were collected. In a few cases, when a sufficient mass of tadpoles could not be obtained during sampling, a nearby water body was sampled instead. Water bodies were generally small (median 0.24 ha, range 0.03 – 10.12 ha) and shallow (maximum depth median 1.5 m, range 0.1 – 14.5 m; Supplemental Data, Table S1). They ranged in elevation from 2786 to 3375 m, and in linear distance from the Valley edge from 42.9 to 82.5 km (Fig. 1; Supplemental Data, Table S1 and Fig. S1). Information for *P. regilla* distribution and water body characteristics was obtained from a survey of all water bodies in the Parks conducted between 1997 and 2002 ([14]; R.A. Knapp, unpublished data).

Sample collection and analysis

The snowpack from the winter of 2004 to 2005 was greater than normal in the Sierra Nevada, resulting in later ice-off for study sites than usual. Air sampling devices were initially deployed between June 30 and July 14, 2005, around the time of ice-off for most of the sites. We collected samples for air, sediment, and tadpoles approximately 30 d later for each site during July 30 to August 12 (period 1), and again approximately 30 d after that between August 29 to September 12 (period 2). The 14 areas were accessed by helicopter. The sequence of sampling during each sampling period was not random, but was designed so there would not be a north-south or east-west pattern to the sequence among the 14 areas.

Contaminant concentrations in air were measured using passive sampling devices consisting of a 1.2 cm × 13.5 cm diameter polyurethane foam (PUF) disk suspended within a metal chamber that allows a consistent exchange between the disk and ambient air [20–22]. The remote nature of sampling stations necessitated air sampling methods which did not require electrical power. Two devices were attached to trees within 100 m of each other at one water body in each of the 14 areas, approximately 2 m above the ground. Field blanks were

exposed to air at the sites (three per sampling period) for approximately 2 min while PUF disks were prepared for deployment; blanks were extracted and analyzed in an identical fashion to samples. Temperature within the air samplers was recorded at hourly intervals using a WatchDog Data Logger (Model 100, Spectrum Technologies). Polyurethane foam disks were deployed in samplers for approximately 30 d for each sampling period. Three isotopically-labeled chemicals, $^{13}\text{C}_6$ -hexachlorobenzene, diazinon (diethyl- d_{10}), and d_4 - α -endosulfan, were spiked on each disk prior to deployment, and recoveries of these chemicals along with their octanol-air partition coefficients K_{OA} were used to estimate the effective air sample volumes. Prior to and after deployment, PUF disks were sealed in glass jars with Teflon[®] lid liners on dry ice, or frozen in the laboratory at $\leq -20^\circ\text{C}$. Sampling shelters were cleaned with chromatographic-grade acetone prior to initial deployment and between sample periods. Details of media preparation, extraction of the PUF disks, analysis methods, estimated detection limits (EDL), and calculations of concentrations in air are described in the Supplemental Data (text and Table S2).

Target analytes for air samples consisted of 27 current-use agricultural pesticides, banned organochlorines, and polybrominated diphenyl ethers (Supplemental Data, Table S2). Laboratory and field blanks did not contain any interfering peaks, and detection limits ranged from 0.5 ng for fipronil, and 18 ng for chlorothalonil (Supplemental Data, Table S2). For statistical analysis, PUF samples in which the content of a chemical was below the EDL were assigned a concentration value computed using half of the EDL and the averages for temperature and air volume for samples in which the chemical was detected.

We collected two sediment cores (4.7-cm diameter, top 2.5 cm of sediment) at 1-m water depth in each water body, or at the deepest point if depth was < 1 m, with a hand corer (2424-A series; Wildlife Supply). Cores were combined in a cleaned 250-ml glass jar with Teflon lid liner, placed immediately on dry ice, and subsequently held in the laboratory at $\leq -20^\circ\text{C}$ until analyzed. Sediment samples were processed and analyzed as described in Usenko et al. [23], with the exception of total organic carbon. Briefly, sediment samples were ground with sodium sulfate (Na_2SO_4), labeled surrogate standards were added, and samples were extracted using pressurized liquid extraction (ASE 300, Dionex) with dichloromethane as a solvent. Interferents were removed from sample extracts using silica cleanup and gel permeation chromatography. Labeled internal standards were added to the final reduced extracts. A laboratory blank was included for each set of 6 to 8 sediment samples. Target analytes included 46 pesticides or their metabolites, 17 polycyclic aromatic hydrocarbons (PAHs), and 6 PCBs. Sediment EDLs for these chemicals are provided in the Supplemental Data, Table S3. Total organic carbon was analyzed for 0.2 g dried subsamples using a CNS-2000 Element Analyzer (LECO). Chemical concentrations in sediment were summarized on a dry-mass basis and carbon basis (ng/g), but subsequent statistical analyses were conducted using the carbon basis because the inorganic content of sediment varied widely among samples and our chemicals of interest partition to the organic component of the sediment. Chemical concentrations with laboratory blank levels exceeding 33% of the measured value were omitted. The frequency of duplicate samples was 10%. Water samples collected concomitantly with sediment samples were analyzed for pH and electrical conductivity in the laboratory following methods used in Bradford et al. [24].

Tadpoles were collected by dip net at each site and placed in plastic bags with lake water. Tadpoles (5 to 10 g) were transferred by hand using powder-free latex gloves to a 25-ml certified pre-cleaned glass vial with Teflon lined cap, wrapped in synthetic padding, and placed on dry ice. Vials were stored on dry ice or in a freezer at -20°C until analysis. Analytical extraction and cleanup procedures and EDLs are provided in Stanley et al. [25]. Briefly, chemical analyses for tadpoles were performed using a matrix solid phase dispersion method in which 2 g of tadpole tissue was ground with 10 g of octadecylsilyl

(C18) and 35 g of sodium sulfate (Na_2SO_4), labeled surrogate standards were added, mixture was packed into a 60-ml solid phase extraction column, and extraction was performed under a vacuum with acetonitrile as a solvent. Sample extracts were reduced, and silica cleanup was performed, followed by a final reduction step and addition of labeled internal standards. A laboratory blank was included with each batch of samples (8–12) extracted. Analytes included 48 pesticide compounds, 17 PAHs, and 7 PCBs. Concentrations are summarized on the basis of wet mass, dry mass, and lipid mass, but subsequent statistical analyses reported herein are for dry-mass basis only. As for sediment, chemical concentrations with laboratory blank levels exceeding 33% of the measured value were omitted, and duplicate sample frequency was 10%. Tadpoles were identified to developmental stage (Gosner stage, [26]) from a sample of approximately 16 tadpoles collected simultaneously with those above (D.W. Sparling, unpublished data). Only tadpoles of Gosner stage ≤ 41 are reported herein.

Sediment and tadpole samples were analyzed using an Agilent 6890 gas chromatograph / 5973N mass spectrometer in both electron impact and electron capture negative ionization modes and selected ion monitoring was used. Calibration curves were solvent based, instruments were monitored using solvent standards (a standard was analyzed for every 3 – 4 samples), and maintenance was performed and new curves were prepared as necessary. Analyte detections were confirmed using the following criteria: 3:1 signal to noise ratio, retention time match (± 0.5 minute with the standards), and matching ion ratios ($\pm 20\%$ abundance). Sediment and tadpole sampling equipment was handled with powder-free latex gloves, cleaned between sites with a solution of Micro 90 cleaning solution (Cole-Parmer), and disinfected between sites with a 1% solution of Quat-128 (Waxie Sanitary Supply) or high-performance liquid chromatography-grade methanol. Sampling equipment was rinsed with lake water prior to sampling at each site. Field blanks were not collected for sediment or tadpole samples because analyte-free field blank substitutes are not available for these media. Samples were stored in airtight containers immediately following collection until chemical methods were initiated at which time laboratory blanks were used to account for any contamination.

Distance metrics

We calculated two metrics for distance between the study sites and the edge of the San Joaquin Valley: linear and upslope distances. Linear distance is the distance to the closest point on the mountain-valley boundary (Fig. 1). Upslope distance was calculated using Arc Info (ESRI, Fig. 1) as the path water would flow from the sampling site to the mountain-valley boundary. Upslope distance based on water flow path was used as a surrogate for the flow path taken by daily upslope winds (mountain winds) typical for the southern Sierra Nevada during summer [27,28]. Linear distance and upslope distance were not significantly correlated among sites, and linear distance but not upslope distance was significantly correlated with elevation (Pearson $r = 0.5072$, $p = 0.0056$, $n = 28$; Supplemental Data, Fig. S1 and Table S1).

Statistical analysis

For values $< \text{EDL}$, the value was replaced with half of the EDL (for air, see further details above). Values for duplicate samples for sediment and tadpoles were averaged, except in a few cases where one of the duplicates was not useable due to high blank level, in which case the other duplicate value was used as the site value.

Unless otherwise stated, statistical analyses were conducted on all values (i.e., detects and nondetects) using nonparametric tests because values were often not normally distributed even with transformation. Multivariate analyses were conducted for detected values only

using parametric techniques. For tadpoles, differences in concentration between sampling periods were evaluated in two ways. First, analysis of covariance (ANCOVA, detects only) was run for each chemical with developmental stage as a covariate. Values were $\log_{10}$ transformed and outliers were removed in two cases to achieve normality of residuals (Shapiro Wilks test). Second, Spearman rank tests were conducted for all values (i.e., detects and nondetects).

Principal components analysis (PCA) was used for all values to evaluate associations in concentrations among chemicals for sediment and tadpoles (detection frequency > 30%), grouped as pesticides or non-pesticides (i.e., PCBs and PAHs). Principal components analysis was used to composite the chemicals into a reduced number of variables (e.g., principal components PC_1, PC_2, and PC_3) that account for as much of the variability in the original variables (i.e., chemical concentrations) as possible. For tadpoles, developmental stage was added to the chemical variables in the PCA. The contribution of each chemical and tadpole stage is represented by its load in each principal component.

Relationships between concentrations and distance from the San Joaquin Valley and elevation were evaluated in two ways. First, for detected values only, stepwise regression was run for all combinations of the chemical metric (i.e., chemical concentration or PC_1 from PCA analyses), distance metric (linear or upslope distance), medium (air, sediment, or tadpole), and sampling period (period 1 or 2). The basic model was chemical metric = distance metric + elevation. Elevation was included because it was positively correlated with linear distance (see above; Supplemental Data, Fig. S1). For tadpoles, three additional terms were included in the model: stage, distance metric $\times$ stage, and elevation $\times$ stage. Stage was included in the analyses because it was significantly correlated with concentrations of some chemicals (see Results and Discussion *section*), and for period 2, it showed significant positive relationships with both linear distance ($n = 27$, $r^2 = 0.1854$, $p = 0.0250$) and upslope distance ($r^2 = 0.2237$, $p = 0.0127$). Data for individual chemicals were log-transformed or square-root transformed, with outliers removed in a few cases, to achieve normality (Shapiro Wilks test). The entry probability for each variable was 0.3 and the probability for retention in the final model was 0.05. Second, for all values (i.e., detects and nondetects), concentration-distance relationships were evaluated using Spearman rank test. Sample sizes are provided in the Supplemental Data, Tables S4 and S6.

The significance level for all statistical tests was $\alpha = 0.05$. An α of 0.05 was deemed appropriate for tests of the many combinations of chemical, medium, and time because our goal was to evaluate the generality of resulting patterns across the numerous combinations, and not to evaluate the significance of each individual combination. Statistical analyses were performed using SAS 9.1.3 (SAS Institute).

RESULTS AND DISCUSSION

Chemicals detected

Chemicals in air—Of the 27 analytes measured in air, only β -endosulfan was detected more than once (Fig. 2). Detection frequency was 41% for period 1 and 57% for period 2, a difference that was not statistically significant ($p[\chi^2] > 0.05$). Variation in β -endosulfan concentrations averaged less within site (2 samples per site) than the overall variation during both sample periods. Specifically, within-site coefficient of variation (CV) averaged 18.8% ($n = 13$ pairs) and 40.2% ($n = 14$ pairs) during Periods 1 and 2, respectively, whereas overall CVs were 100.2% ($n = 27$) and 90.9% ($n = 28$), respectively. Temperature within the air samplers averaged 15.0 ± 0.2 (SE) °C and 11.5 ± 0.3 °C for periods 1 and 2, respectively. The calculated volume of air sampled averaged 377 ± 24 (SE) m³ and 302 ± 19 m³ for the two sampling periods, respectively.

Chlorpyrifos and diazinon were each detected in only one sample (chlorpyrifos, Area H, period 1; diazinon, Area D, period 2). None of the other analytes were detected above estimated detection limits. Since degradation of diazinon-diethyl-d₁₀ was observed from the depuration chemical experiment (see Supplemental Data), calculation of chlorpyrifos and diazinon concentrations could not be accurately determined.

Detection of the β -endosulfan isomer in these air samples but not the α -endosulfan isomer was an unexpected result since α -endosulfan is dominant in the technical pesticide mixture [29] and is typically more frequently detected in air while β -endosulfan is more frequently detected in precipitation. An expanded effort to measure air concentrations of pesticides and other pollutants at the study sites is needed to further explore atmospheric deposition sources to this remote region.

Chemicals in sediment—Thirty-three chemicals were detected in sediment. Fifteen of these were selected for comparison because their detection frequency was $\geq 30\%$ during at least one of the two sampling periods (Fig. 3, Supplemental Data, Table S4). Retene was excluded because it can originate from both natural and anthropogenic sources [30]. The 15 chemicals consisted of nine pesticides or their degradation products (5 were used in 2005, 4 were banned), and six non-pesticides (4 PCBs and 2 PAHs). Detection frequency during a sampling period ranged from 11 to 100% (median 83%; Supplemental Data, Table S4). Concentrations of all chemicals were very low, averaging < 12 ng/g dry mass and < 160 ng/g carbon (Supplemental Data, Table S4). Total organic carbon content of sediment averaged 10.5 ± 1.0 (SE) % dry mass, but varied widely (range, 0.4 – 29.2 %; $n = 56$).

Coefficients of variation for duplicate samples (i.e., 3 pairs taken at the same site for period 1, 6 pairs for period 2) averaged less than CVs for all samples for all chemicals during each sampling period. Within-area CVs for chemical concentration (i.e., two sites per area) averaged less than the CVs for all sites for all chemicals during each sampling period. However, within-area CVs were generally large relative to CVs for all sites (mean fraction 0.565, range, 0.188 – 0.916), indicating that a large fraction of variation among samples occurred between the two sites within each area. Electrical conductivity and pH of water are provided in the Supplemental Data, Table S5.

Chemicals in tadpoles—A total of 18 chemicals were detected in tadpoles. Twelve of these were selected for comparison because their detection frequency was $\geq 30\%$ during at least one of the two sampling periods (Fig. 3, Supplemental Data, Table S6). Retene was excluded for the same reason it was for sediment. The 12 chemicals consisted of the same nine pesticide chemicals as those detected in sediment (but only eight during period 2, when chlorpyrifos was absent), along with three PCBs. Detection frequency during a sampling period ranged from 0 to 100% (median 74%; Supplemental Data, Table S6). Concentrations of all chemicals were very low, averaging < 1 ng/g wet mass, < 8 ng/g dry mass, and < 300 ng/g lipid (Supplemental Data, Table S6). Lipid content averaged 3.5 ± 0.4 (SE) % dry mass (range 0.3 to 7.3 %; $n = 27$) during period 1 and 8.0 ± 0.6 % (range 2.6 to 14.7 %; $n = 27$) during period 2. Median tadpole developmental stage per sample averaged 31.5 ± 0.6 (SE; range 26 to 37; $n = 27$) during period 1 and 36.6 ± 0.4 (range 30 to 39.5; $n = 26$) during period 2.

The CVs for duplicate samples (i.e., 2 pairs taken at the same site for period 1, 2 pairs for period 2) averaged less than CVs among all samples for all chemicals during each sampling period, except for chlorpyrifos and PCB 153 during period 1. Within-area CVs for chemical concentration averaged less than CVs for all sites for nearly all chemicals during each sampling period. The exceptions were chlorpyrifos and trans-nonachlor during period 1 and trans-chlordane during period 2. As with concentrations in sediment, within-area CVs were

generally large relative to CVs among all sites (mean fraction 0.725, range, 0.301 – 1.030), indicating that a large fraction of variation among samples occurred between the two sites within each area.

Differences in concentrations between sampling periods

Chemical concentrations for a number of chemical/media combinations were greater for period 2 than period 1. For air, β -endosulfan concentrations were significantly greater during period 2 ($n = 27$) than period 1 ($n = 28$; Wilcoxon 2-sample test, $p = 0.0004$; Fig. 2). Excluding non-detect values, concentrations were twice as much during period 2 (13.3 ± 1.6 [SE] pg/m^3 , $n = 11$) than during period 1 (6.6 ± 1.1 pg/m^3 , $n = 16$; t test, $p = 0.005$).

For sediment, non-pesticide concentrations (ng/g carbon) differed significantly between the two periods for three chemicals based on signed rank tests (data include both detects and nondetects). Specifically, concentrations were higher during period 2 than period 1 for PCB 153 ($n = 25$ pairs; signed rank test; $p = 0.0043$) and PCB 187 ($n = 24$ pairs; $p = 0.0063$), whereas benzo[*b*]fluoranthene concentrations were significantly lower during period 2 ($n = 20$ pairs, $p = 0.0192$). In contrast, no pesticide concentrations differed significantly between the two sampling periods (signed rank test).

For tadpoles, chemical concentrations were significantly higher for period 2 than period 1 for 6 of the 11 chemicals present during both periods (detects only; ANCOVA; α -endosulfan, *trans*-chlordane, *cis*-nonachlor, PCB 187 [Fig. 4]; also *trans*-nonachlor and PCB 183). This difference between sampling periods was not related to lipid content as chemical concentration on a dry-mass basis was significantly related to lipid content only for dacthal (ANCOVA, $p = 0.0261$). Developmental stage showed a significant negative relationship to concentration for 5 of 11 chemicals, with tadpoles at later developmental stages having lower chemical concentrations (α -endosulfan, *trans*-chlordane, and *cis*-nonachlor [Fig. 4], and *trans*-nonachlor and PCB 183). Differences in concentrations in tadpoles between sampling periods were also evident based on analyses that included both detects and nondetects. Concentrations were greater during period 2 than period 1 for five chemicals, but the opposite was found for chlorpyrifos, which was not detected during period 2 (signed rank tests). A chemical concentration was significantly negatively related to stage only for PCB 183 during period 1 (Spearman rank test).

Although the explanation for generally greater concentrations in tadpoles of historic-use chemicals during period 2 than period 1 is unknown, the greater concentrations during period 2 for the current-use β -endosulfan in air and α -endosulfan in tadpoles, and detection of chlorpyrifos only during period 1, may be due to patterns of pesticide use in the San Joaquin Valley. Application of chlorpyrifos in the Valley is consistent with this prediction, because approximately twice as much pesticide was applied during period 1 than period 2, and amounts were decreasing for several weeks before and during period 2 (California Department of Pesticide Regulation Pesticide Use Reports). For endosulfan, however, application in the Valley showed a pattern opposite that expected. Specifically application during the 30-d deployment interval for air samples averaged 45% greater for period 1 than for the corresponding interval for period 2 (California Department of Pesticide Regulation Pesticide Use Reports).

Associations in concentrations among media

Chemical concentrations in sediment and tadpoles showed a limited degree of correlation with each other. During Period 2, concentrations for four of 11 chemicals present in both media were positively correlated (*p,p'*-DDE, β -endosulfan, endosulfan sulfate, and PCB 183; detects and nondetects; $n = 18$ to 26; Spearman rank correlation). During period 1,

however, none of the 12 chemicals found in both sediment and tadpoles were significantly correlated ($n = 7 - 27$; Spearman rank correlation). Concentrations of β -endosulfan in air were not significantly correlated with concentrations in sediment or tadpoles for either period 1 or 2 ($n = 14$ sites in each comparison; Spearman rank correlation test).

Composition of chemical suites

The composition of chemical suites was similar among sites. For both sediment and tadpoles, for both sampling periods, many (32 – 73%) pairwise comparisons among the chemicals showed significant positive correlations, and none showed a significant negative relationship (detects and nondetects; Spearman rank correlation). In the seven PCAs for pesticide and non-pesticide concentrations in sediment and tadpoles over two sampling times, all chemicals loaded positively on principal component 1 (PC_1), and the eigenvalues for PC_1 (i.e., fraction of total variation explained by PC_1) were relatively high (0.58 – 0.74 for sediment and 0.44 to 0.66 for tadpoles; $n = 17$ to 28; Supplemental Data, Fig. S2 and Table S7). Thus, PC_1 represents chemicals in general for each PCA, and this component is used as a metric to evaluate patterns for chemicals as a group in several analyses below. Moreover, the majority of chemicals in each PCA had similar loading values on PC_1 (Supplemental Data, Fig. S2 and Table S7), further indicating similar composition among sites. Such similarity in chemical composition across sites suggests that chemical transport patterns (e.g., chemical mixtures transported and their temporal variation) have been similar among the sites. For example, if amounts of the each chemical transported had varied randomly among the sites, loadings on PC_1 in each PCA analysis should have included both negative and positive values, with highly variable loadings among chemicals.

Associations between concentrations and distance from the San Joaquin Valley

Air— β -endosulfan concentration in air was not significantly related to either linear or upslope distance for either sampling period in the stepwise regressions (Fig. 2). However, when non-detect values were included, a significant negative relationship with one distance metric (upslope distance) was evident during period 1 (Fig. 2A; Spearman rank correlation, $p = 0.015$). **Sediment.** A general relationship between chemical concentrations in sediment and distance from the Valley was not apparent, but there was some evidence for a distance effect in both the stepwise regressions (detects only) and Spearman rank tests (detects and nondetects). Stepwise regressions were significant for one chemical group and several individual chemicals, but patterns for the two sampling periods differed substantially (Table 1). Only one chemical (chlorpyrifos) was significantly related to a distance metric during period 1 (i.e., upslope distance, positively), whereas a number of relationships were significant for period 2. During period 2, significant relationships with linear distance were shown for PC_1 for non-pesticides, all four individual PCBs, and four individual pesticide chemicals (i.e., endosulfan sulfate, *trans*-chlordane, and *cis*- and *trans*-nonachlor; Table 1; Fig. 5A and B). In contrast, three pesticide chemicals showed significant positive relationships with upslope distance (chlorpyrifos, dacthal, β -endosulfan; Table 1; Fig. 5C and D). Spearman rank test results (Supplemental Data, Table S8) were generally similar to those for stepwise regressions. In particular, chemical concentrations were significantly related to a distance metric almost exclusively in period 2, and the significant relationships during period 2 were predominantly negative with linear distance. **Tadpoles.** As for sediment, a general relationship between chemical concentrations in tadpoles and distance from the Valley was not evident, but there was evidence for a distance effect in a few of the stepwise regressions (detects only) and Spearman rank tests (detects and nondetects). In stepwise regressions, no relationship with a distance metric was significant for period 1, whereas several were significant for period 2 (Table 1). The significant relationships during period 2 were negative with upslope distance for PC_1 for pesticides, PC_1 for non-pesticides, and α -endosulfan (Table 1; Fig. 5E-F and Supplemental Data, Fig. S3). The

distance relationships for these three chemical metrics in tadpoles all differed from those found for these metrics in sediment for the same sampling period; that is, in sediment the relationships were either not significant or were related to linear distance instead of upslope distance. Among other factors in the stepwise regressions for tadpoles, stage showed a significant negative relationship to concentration for three chemicals during period 1 (β -endosulfan, *cis*-nonachlor, *trans*-nonachlor). Spearman rank test results were generally similar to those for stepwise regressions (Supplemental Data, Table S8). In particular, significant distance relationships were much more frequent for period 2 than period 1, and the significant relationships found during period 2 were all negative with upslope distance.

Geographic patterns of chemical concentrations at high-elevation

A consistent pattern of chemical concentrations with distance from the San Joaquin Valley was not found among chemicals, media, or time, either as a function of linear distance or upslope distance. Nevertheless, there was limited support for the hypothesis that chemical concentrations decrease with distance from the Valley. A negative upslope-distance relationship was evident for air (i.e., β -endosulfan during period 1) and for tadpoles (i.e., PC_1 for both pesticides and non-pesticides during period 2). In contrast, a negative linear-distance relationship was found for non-pesticides in sediment (i.e., stepwise regressions for PC_1 for non-pesticides and four individual PCBs during period 2). Individual pesticides in sediment during period 2 showed conflicting relationships with the two distance metrics, and some of these relationships were negative whereas others were positive. Thus, it remains ambiguous whether linear or upslope distance is the more relevant metric. Also, even in cases where a chemical-distance relationship was significant, the variance explained by the relationship was generally low (i.e., low r^2 ; Table 1) and the magnitude of the significant distance effects was on the order of 3-fold or less (Fig. 5).

A significant elevation effect that was independent of distance in stepwise regressions occurred only for one of the 58 chemical metric/medium/time combinations. This was *p,p'*-DDE in tadpoles, period 2, which decreased with elevation.

Assuming a negative distance-exposure relationship, Davidson and Knapp [14] developed a distance-weighted metric to represent extent of upwind pesticide use for sites in the southern Sierra Nevada. Their metric represented all pesticides applications over a 10-year period, and yielded isolines in Sequoia and Kings Canyon National Parks that corresponded fairly closely to lines of equal linear distance from the San Joaquin Valley (Fig. 1 in Davidson and Knapp [14]). Such a neat pattern of decline with distance was not found for pesticide concentrations within our high-elevation study area, which ranged from 43 to 82 km from the Valley.

The present study suggests that transport processes are important in determining the chemical composition at high elevation sites, but not in determining the differences in concentrations among sites. Chemical compositions were generally similar among sites (as evidenced by PCA analyses), which could be explained by the delivery of similar chemical mixtures to the sites. In contrast, if transport processes (e.g., dilution by air mixing and photochemical degradation during transit) were responsible for differences in concentrations among sites, the variation in concentrations among nearby sites should have been much less than variation among sites far from each other. Moreover, the relationships between concentrations and our geographic metrics should have been generally consistent among the many chemical/medium/time combinations. Neither of these situations prevailed in this study.

Geographic patterns across the Sierra Nevada

For the entire distance from the San Joaquin Valley edge to the Sierra Nevada crest, variations in chemical concentrations observed in the present study at high elevation appear to be minute in comparison to concentration differences between the Valley and the nearest high elevation sites. Among the chemicals and media analyzed in the present study, three have been reported from sites closer to the Valley at lower elevations in the southern Sierra Nevada (Kaweah watershed): β -endosulfan in air [5] (Fig. 6A), and *p,p'*-DDE and chlorpyrifos in *P. regilla* tadpoles [4,31] (Fig. 6C, D). In addition, concentrations of seven pesticides have been measured in surface water from sites across the Valley-to-crest gradient that includes the study area [5,9,32]. These are chlorothalonil, chlorpyrifos, α - and β -endosulfan (Fig. 6B), diazinon, malathion, and trifluralin. During summer months, concentrations of all these chemical/media combinations decreased substantially between the Valley edge at low elevation and the nearest high-elevation sites 42 km linear distance (62 km upslope distance) from the Valley (Fig. 6). In contrast, all sites beyond 42 km (62 km upslope distance) were at high elevation and demonstrated very low concentrations that did not decrease appreciably with distance.

The geographic differences in concentrations for current-use pesticides represented in Figure 6, chlorpyrifos and endosulfan, were not likely due to differences among years of study because the amounts used in the San Joaquin Valley during the June to September period (California pesticide use reports) varied among years by only a small fraction of the variation in concentrations represented across the Valley-to-crest gradient. Thus, although contaminant concentrations generally decrease substantially from the Valley to the crest (present study, [8,10]), most of this decrease in the study region appears to take place along the distance/elevation gradient up to 42 km from the Valley where elevation is approximately 2800 m. Indeed, for the few chemical/media/time combinations that showed a significant relationship with distance at high elevation in the present study, the 3-fold or less magnitude of this effect may be miniscule in comparison to the decline in concentrations from 0 to 42 km from the Valley edge.

The breakpoint in the distance-concentration gradient at 42 km linear distance (~ 2800 m elevation) suggests that nonlinear processes dominate in determining contaminant concentrations between the San Joaquin Valley and the crest of the mountain range. These processes, such as dilution of contaminants during atmospheric transport, could be related to both distance and elevation. The relative contributions of these two variables in explaining the 42-km threshold, however, are not clear. Over a much larger portion of the Sierra Nevada, however, Angermann et al. [8] found that elevation and not distance was a significant factor in stepwise regressions for concentrations of toxaphene and PCBs. It is plausible that elevation is the predominant factor in the study region because air-flows during summer at higher elevations are intermittently decoupled from air flows at lower elevations [27]. Nevertheless, the predominant air-flow pattern in the mountains during summer is for daily up-valley winds originating from near the edge of the San Joaquin Valley [27,28]. A tracer study showed steady dilution of the tracer in air during transport along the distance/elevation gradient in the Kaweah watershed [28], but additional studies would be required to determine if the apparent 42-km threshold is consistent with dilution in air and whether distance or elevation is the better explanatory variable.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

We are most grateful to Joanna Christion and Amanda Marusich of Sequoia and Kings Canyon National Parks (SEKI) for meticulously conducting much of the field sampling, and to Harold Werner, Danny Boiano, and Annie Esperanza also of SEKI for facilitating the project in many ways. We also thank Hassan Basagic, Chad Cross, Rebecca Rising, Krystal Ward, and Carrie Vernon and other members of the SEKI helicopter crew for considerable help. We are grateful to Roland Knapp for sharing results for wetland/amphibian field surveys, Donald Sparling for provided tadpole staging data, and Carlos Davidson for discussing the project. James Seiber, Thomas Cahill, Walter Jarman, and Lara Hansen kindly reviewed the research plan for the project, and Paula Allen, Deborah Chaloud, and Donald Sparling provided comments on earlier versions of the manuscript. The research described herein was funded by the U.S. Environmental Protection Agency (U.S. EPA) through Interagency Agreement DW14989008 with the National Park Service, and the U.S. National Institute of Environmental Health Sciences (grant P30ES00210). The article has been approved for publication by the U.S. EPA.

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Fig. 1. Sample site locations (triangles) in Sequoia and Kings Canyon National Parks (CA, USA) (purple outline). Letters (A, B, etc.) refer to 14 areas containing sample sites. Black outline shows watersheds of Kings, Kaweah, and Kern Rivers. Red dashed line indicates the boundary between mountainous terrain and San Joaquin Valley. Colored bands indicate upslope distance (see text) from Valley in 25-km increments, indicated by numbers (25, 50, etc.).

Fig. 2. β -endosulfan concentration in air as a function of upslope distance from the San Joaquin Valley during periods 1 (**A**) and 2 (**B**). Solid circles indicate values above estimated detection limit (EDL); open triangles indicate samples below EDL. Values assigned for samples below EDL are 1.34 pg/m³ for period 1 and 1.74 pg/m³ for period 2 (see text). Numerals indicate multiple samples for point. Regression lines and statistics shown apply to detected values (circles; NS indicates $p < 0.05$). Non-parametric correlation for all values (detects and nondetects) was significant only for period 1 (A; Spearman rank test, $p = 0.015$).

Fig. 3. Chemical concentrations in sediment (**A**) and tadpoles (**B**). Values below estimated detection limits (EDL) were replaced with half of the EDL. Data shown are median (horizontal line within box) and 25th and 75th percentiles (box limits). Open boxes indicate period 1; hatched boxes indicate period 2. Sample sizes, detection frequencies, and concentrations calculated on dry mass basis for sediment, wet basis for tadpoles, and lipid normalized for tadpoles are provided in the Supplemental Data, Tables S3 and S5.

Fig. 4. Chemical concentrations in tadpoles for selected chemicals as a function of tadpole developmental stage during period 1 (solid circles) and period 2 (open triangles). Regression lines (solid line for period 1; dashed line for period 2) are shown with a common slope because the stage $\times$ period interaction term in all analysis of covariance analyses was not significant (NS). Data used are detects only. (A) α -endosulfan I. (B) *Trans*-chlordane (one outlier removed). (C) *Cis*-nonachlor. (D) PCB 187. PCB = polychlorinated biphenyls.

Fig. 5. Selected significant relationships between chemical concentrations or principal component 1 and distance metrics in stepwise regressions, all during period 2. PCBs/PAHs refer to polychlorinated biphenyls and polycyclic aromatic hydrocarbons. The r^2 and p values are provided in Table 1.

Fig. 6.

Concentrations of pesticide compounds as a function of linear distance from the San Joaquin Valley edge within the Kaweah, Kings, and Kern watersheds. Months represented are June through September of various years. Values less than the estimated detection limit (EDL) are shown as half of the EDL. **(A)** α -endosulfan in air; symbols and data sources: open triangles [5], closed circles (present study). **(B)** α -plus β -endosulfan in surface water; open triangles [5,9], open squares [32]. **(C)** p,p' -DDE (dichlorodiphenyldichloroethylene) in *Pseudacris regilla* tadpoles; open triangles [4], open diamonds [31], solid circles (present study). **(D)** Chlorpyrifos in *P. regilla* tadpoles; open triangles [4], solid circles (present study).

Table 1

Results from stepwise regressions for chemical concentrations (detects only) and principal component 1 (PC_1) as a function of distance metrics (linear and upslope distance) for sediment and tadpoles. PC_1 is derived from separate principal component analyses for all pesticides and all polychlorinated biphenyls/polycyclic aromatic hydrocarbons (PCB/PAHs; detects and nondetects). Samples sizes for individual chemicals ranged from 6 to 28 (median 20; Supplemental Data, Tables S4 and S6) and for PC_1 ranged from 17 to 28 (median 24; Supplemental Data, Table S7). Values shown for significant relationships are r^2 /direction of relationship (p value for slope $\neq 0$). NS indicates not significant. (---) indicates chemical is not in dataset or detection frequency was <30% (Supplemental Data, Tables S4 and S6). DDE refers to dichlorodiphenyldichloroethylene.

	Period 1				Period 2			
	Sediment		Tadpoles		Sediment		Tadpoles	
	Linear	Upslope	Linear	Upslope	Linear	Upslope	Linear	Upslope
Pesticides								
All Pesticides (PC_1)	NS	NS	NS	NS	NS	NS	NS	0.397/– (0.001)
Chlorpyrifos	NS	0.677/+ (0.044)	NS	NS	NS	0.297/+ (0.009)	---	---
Dacthal	NS	NS	NS	NS	NS	0.210/+ (0.028)	NS	NS
α -endosulfan	NS	NS	NS	NS	---	---	NS	0.592/– (0.002)
B-endosulfan	NS	NS	NS	NS	NS	0.286/+ (0.003)	NS	NS
Endosulfan sulfate	NS	NS	NS	NS	0.202/– (0.017)	NS	NS	NS
<i>p,p'</i> -DDE	NS	NS	NS	NS	NS	NS	NS	NS
<i>Trans</i> -chlordane	NS	NS	NS	NS	0.178/– (0.045)	NS	NS	NS
<i>Cis</i> -nonachlor	NS	NS	NS	NS	0.241/– (0.011)	NS	NS	NS
<i>Trans</i> -nonachlor	NS	NS	NS	NS	0.405/– (0.001)	NS	NS	NS
<i>Non-Pesticides</i>								
All PCB/PAHs								
(PC_1)	NS	NS	---	---	0.253/– (0.006)	NS	NS	0.185/– (0.028)
PCB 138	NS	NS	---	---	0.225/– (0.012)	NS	---	---
PCB 153	NS	NS	NS	NS	0.323/– (0.004)	NS	NS	NS
PCB 183	NS	NS	---	---	0.305/– (0.018)	NS	NS	NS
PCB 187	NS	NS	NS	NS	0.364/– (0.001)	NS	NS	NS
Benzo[b]fluoranthene	NS	NS	---	---	---	---	---	---
Fluoranthene	NS	NS	---	---	NS	NS	---	---