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SPATIAL PATTERNS OF ATMOSPHERICALLY DEPOSITED ORGANIC CONTAMINANTS AT HIGH-ELEVATION IN THE SOUTHERN SIERRA NEVADA MOUNTAINS, CALIFORNIA

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Abstract -- Atmospherically deposited contaminants in the Sierra Nevada mountains of California have been implicated as adversely affecting amphibians and fish, yet the distributions of contaminants within the mountains are poorly known, 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 to 3375 m elevation; 43 to 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/m^3 for β-endosulfan in air. Principal components analysis indicated that chemical compositions were generally similar among sites, suggesting that chemical transport patterns were also 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

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, contaminant distributions within the mountains are poorly known, 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

78 elevation, however, can be difficult because the two factors are often correlated in gradient
79 studies, i.e., elevation increases as distance from a source increases [17]. In the southern Sierra
80 Nevada, though, the alpine zone extends to over 30-km wide and offers an opportunity to
81 evaluate the influence of distance on contaminant concentrations while holding elevation more-
82 or-less constant.

83 Several studies in the Sierra Nevada mountain range have examined concentrations of
84 airborne pesticides in various media along distance/elevation gradients from the adjacent San
85 Joaquin Valley (i.e., southern arm of the Central Valley; [1,2,5,7,8,10]). In general,
86 concentrations of pesticides and PCBs decreased along these gradients, although relatively few
87 sites were represented from high elevation (i.e., >3000 m). However, limited data from three
88 studies [8-10] also suggest a decrease in pesticide and PCB concentrations with distance from the
89 Valley even within the high-elevation zone. Davidson and Knapp [14] provide a predictive
90 framework for evaluating pesticide distributions in the southern Sierra Nevada mountain range
91 by showing that a metric for extent of upwind pesticide use decreases monotonically with
92 distance from the Valley.

93 To better understand distribution patterns for chemical contaminants in the mountains,
94 the present study tested the hypothesis that concentrations of atmospherically deposited
95 chemicals at high elevation in the southern Sierra Nevada mountain range decrease with distance
96 from the San Joaquin Valley. Our goal was to evaluate the generality of resulting patterns with
97 distance across many chemicals (including both current- and historic-use pesticides), three media
98 (air, sediment, and tadpoles), and two sampling periods. The influence of tadpole developmental
99 stage on chemical concentrations in tissue was evaluated and included in the analyses for
100 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), 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 our results 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 to 2.8 km). *Pseudacris regilla* was selected for sampling because it is widespread and abundant throughout the study area, and it is an aquatic breeding frog like *R. muscosa* and *R. sierrae*. 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 to 10.12 ha) and shallow (maximum depth median 1.5 m, range 0.1 to 14.5 m; 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; Table S1; 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 2004-2005 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 x 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, Inc., Elysburg, PA). PUF disks were deployed in samplers for approximately 30 d for each sampling period. Three isotopically-labeled chemicals, $^{13}C_6$-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 $\leq -20\ ^{o}C$. 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 Supporting Information (text and Table S2).

Target analytes for air samples consisted of 27 current-use agricultural pesticides, banned organochlorines, and polybrominated diphenyl ethers (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 (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 ½ 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 Co., Buffalo, NY). 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 ≤ -20 ^{o}C until analyzed. Sediment samples were processed and analyzed as described in [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, Sunnyvale, CA) 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 polychlorinated biphenyls (PCBs). Sediment EDLs for these chemicals are provided in Table S3. Total organic carbon was analyzed for 0.2 g dried subsamples using a CNS-2000 Element Analyzer (LECO Corp., St. Joseph, Michigan). 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

192 with sediment samples were analyzed for pH and electrical conductivity in the laboratory
193 following methods used in Bradford et al. [24].

194 Tadpoles were collected by dip net at each site and placed in plastic bags with lake water.
195 Tadpoles (5 to 10 g) were transferred by hand using powder-free latex gloves to a 25-ml certified
196 pre-cleaned glass vial with Teflon lined cap, wrapped in synthetic padding, and placed on dry
197 ice. Vials were stored on dry ice or in a freezer at -20 until analysis. Analytical extraction and
198 cleanup procedures and EDLs are provided in Stanley et al. [25]. Briefly, chemical analyses for
199 tadpoles were performed using a matrix solid phase dispersion method in which 2 g of tadpole
200 tissue was ground with 10 g of octadecylsilyl (C18) and 35 g of sodium sulfate (Na_2SO_4), labeled
201 surrogate standards were added, mixture was packed into a 60-ml solid phase extraction column,
202 and extraction was performed under a vacuum with acetonitrile as a solvent. Sample extracts
203 were reduced, and silica cleanup was performed, followed by a final reduction step and addition
204 of labeled internal standards. A laboratory blank was included with each batch of samples (8-12)
205 extracted. Analytes included 48 pesticide compounds, 17 PAHs, and 7 PCBs. Concentrations
206 are summarized on the basis of wet mass, dry mass, and lipid mass, but subsequent statistical
207 analyses reported herein are for dry-mass basis only. As for sediment, chemical concentrations
208 with laboratory blank levels exceeding 33% of the measured value were omitted, and duplicate
209 sample frequency was 10%. Tadpoles were identified to developmental stage (Gosner stage,
210 [26]) from a sample of approximately 16 tadpoles collected simultaneously with those above
211 (D.W. Sparling, unpublished data). Only tadpoles of Gosner stage ≤ 41 are reported herein.

212 Sediment and tadpole samples were analyzed using an Agilent 6890 gas chromatograph /
213 5973N mass spectrometer in both electron impact and electron capture negative ionization modes
214 and selected ion monitoring was used. Calibration curves were solvent based, instruments were

monitored using solvent standards (a standard was analyzed for every 3 to 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 (± 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, Vernon Hills, IL), and disinfected between sites with a 1% solution of Quat-128 (Waxie Sanitary Supply, San Diego, CA) or HPLC-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, Redlands, CA; 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, and linear distance but not upslope distance was significantly correlated with elevation (Pearson $r = 0.5072$, $p = 0.0056$, $n = 28$; Fig. S1; Table S1).

Statistical Analysis

For values < EDL, the value was replaced with 1/2 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 & PAHs). Principal components analysis was used to composite the chemicals into a reduced number of variables (i.e., 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; Fig. S1). For tadpoles, three additional terms were included in the model: stage, distance metric × stage, and elevation × stage. Stage was included in the analyses because it was significantly correlated with concentrations of some chemicals (see Results and Discussion), 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 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 Inc., Cary, NC).

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 *CV*s were 100.2% (*n* = 27) and 90.9% (*n* = 28), respectively. Temperature within the air samplers averaged 15.0 ± 0.2 (SE) ^{o}C and 11.5 ± 0.3 ^{o}C for Periods 1 and 2, respectively. The calculated volume of air sampled averaged 377 ± 24 (SE) m^3 and 302 ± 19 m^3 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-d_{10} was observed from the depuration chemical experiment (see Supporting Information), 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

306 precipitation. An expanded effort to measure air concentrations of pesticides and other
307 pollutants at the study sites is needed to further explore atmospheric deposition sources to this
308 remote region.

309 Chemicals in Sediment -- Thirty-three chemicals were detected in sediment. Fifteen of
310 these were selected for comparison because their detection frequency was ≥ 30% during at least
311 one of the two sampling periods (**Fig. 3**, Table S4). Retene was excluded because it can
312 originate from both natural and anthropogenic sources [30]. The 15 chemicals consisted of nine
313 pesticides or their degradation products (5 were used in 2005, 4 were banned), and six non-
314 pesticides (4 PCBs and 2 PAHs). Detection frequency during a sampling period ranged from 11
315 to 100% (median 83%; Table S4). Concentrations of all chemicals were very low, averaging <
316 12 ng/g dry mass and < 160 ng/g carbon (Table S4). Total organic carbon content of sediment
317 averaged 10.5 ± 1.0 (SE) % dry mass, but varied widely (range, 0.4 to 29.2 %; n = 56).

318 Coefficients of variation for duplicate samples (i.e., 3 pairs taken at the same site for
319 Period 1, 6 pairs for Period 2) averaged less than *CV*s for all samples for all chemicals during
320 each sampling period. Within-area *CV*s for chemical concentration (i.e., two sites per area)
321 averaged less than the *CV*s for all sites for all chemicals during each sampling period. However,
322 within-area *CV*s were generally large relative to *CV*s for all sites (mean fraction 0.565, range,
323 0.188 to 0.916), indicating that a large fraction of variation among samples occurred between the
324 two sites within each area. Electrical conductivity and pH of water are provided in Table S5.

325 Chemicals in Tadpoles -- A total of 18 chemicals were detected in tadpoles. Twelve of
326 these were selected for comparison because their detection frequency was ≥ 30% during at least
327 one of the two sampling periods (Fig. 3, Table S6). Retene was excluded for the same reason it
328 was for sediment. The 12 chemicals consisted of the same nine pesticide chemicals as those

329 detected in sediment (but only eight during Period 2, when chlorpyrifos was absent), along
330 with three PCBs. Detection frequency during a sampling period ranged from 0 to 100% (median
331 74%; Table S6). Concentrations of all chemicals were very low, averaging < 1 ng/g wet mass, <
332 8 ng/g dry mass, and < 300 ng/g lipid (Table S6). Lipid content averaged 3.5 ± 0.4 (SE) % dry
333 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)
334 during Period 2. Median tadpole developmental stage per sample averaged 31.5 ± 0.6 (SE; range
335 26 to 37; n = 27) during Period 1 and 36.6 ± 0.4 (range 30 to 39.5; n = 26) during Period 2.
336 The *CV*s for duplicate samples (i.e., 2 pairs taken at the same site for Period 1, 2 pairs for
337 Period 2) averaged less than *CV*s among all samples for all chemicals during each sampling
338 period, except for chlorpyrifos and PCB 153 during Period 1. Within-area *CV*s for chemical
339 concentration averaged less than *CV*s for all sites for nearly all chemicals during each sampling
340 period. The exceptions were chlorpyrifos and trans-nonachlor during Period 1 and trans-
341 chlordane during Period 2. As with concentrations in sediment, within-area *CV*s were generally
342 large relative to *CV*s among all sites (mean fraction 0.725, range, 0.301 to 1.030), indicating that
343 a large fraction of variation among samples occurred between the two sites within each area.
344
345 *Differences in Concentrations between Sampling Periods*
346
347 Chemical concentrations for a number of chemical/media combinations were greater for
348 Period 2 than Period 1. For air, β-endosulfan concentrations were significantly greater during
349 Period 2 (n = 27) than Period 1 (n = 28; Wilcoxon 2-sample test, p = 0.0004; Fig. 2). Excluding
350 non-detect values, concentrations were twice as much during Period 2 (13.3 ± 1.6 [SE] pg/m^3, n
351 = 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 including 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 (detect 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 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 (signed rank test), but 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 may be due to patterns of endosulfan use in the San Joaquin Valley. However, the precise source area within the Valley is

unknown, and endosulfan application throughout the Valley showed a pattern opposite that expected. Specifically application during the 30-d deployment periods for air samples averaged greater for Period 1 (5470 kg) than for Period 2 (3762 kg; 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 to 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 to 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

398 chemicals loaded positively on principal component 1 (PC_1), and the eigenvalues for PC_1
399 (i.e., fraction of total variation explained by PC_1) were relatively high (0.58 to 0.74 for
400 sediment and 0.44 to 0.66 for tadpoles; n =17 to 28; Fig. S2 and Table S7). Thus, PC_1
401 represents chemicals in general for each PCA, and this component is used as a metric to evaluate
402 patterns for chemicals as a group in several analyses below. Moreover, the majority of
403 chemicals in each PCA had similar loading values on PC_1 (Fig. S2 and Table S7), further
404 indicating similar composition among sites. Such similarity in chemical composition across sites
405 suggests that chemical transport patterns (e.g., chemical mixtures transported and their temporal
406 variation) have been similar among the sites. For example, if amounts of the each chemical
407 transported had varied randomly among the sites, loadings on PC_1 in each PCA analysis should
408 have included both negative and positive values, with highly variable loadings among chemicals.
409
410 *Associations between Concentrations and Distance from the San Joaquin Valley*
411
412 Air -- β-endosulfan concentration in air was not significantly related to either linear or
413 upslope distance for either sampling period in the stepwise regressions (Fig. 2). However, when
414 non-detect values were included, a significant negative relationship with one distance metric
415 (upslope distance) was evident during Period 1 (Fig. 2A; Spearman rank correlation, p = 0.015).
416 Sediment -- A general relationship between chemical concentrations in sediment and
417 distance from the Valley was not apparent, but there was some evidence for a distance effect in
418 both the stepwise regressions (detects only) and Spearman rank tests (detects and nondetects).
419 Stepwise regressions were significant for one chemical group and several individual chemicals,
420 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 (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 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 (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 for only for one of the 58 chemical metric/medium/time combinations. This was for 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 included 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 (see their Fig. 1). 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. 6 A**), and p,p'-DDE and chlorpyrifos in *P. regilla* tadpoles [4,31] (Fig. 6 C, 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. 6 B), 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 Fig. 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-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

SUPPORTING INFORMATION

Passive Air Sample Sampling and Analysis Method.

Table S1. Detailed information for sites sampled.

Table S2. Target analytes and depuration chemicals included in passive air sample analysis along with analytical parameters, estimated method detection limits, and average spike recovery values.

Table S3. Sediment semi-volatile organic compound estimated detection limits (EDLs) in ng/g dry weight.

Table S4. Chemical concentrations and detection frequencies in sediment.

Table S5. pH and electrical conductivity of water samples.

Table S6. Chemical concentrations and detection frequencies in tadpoles.

Table S7. Principal components analysis (PCA) of chemical concentrations for pesticides and non-pesticides in sediment (carbon basis) and tadpoles (dry-mass basis).

Table S8. Spearman rank correlation test results for chemical concentrations and principal component 1 (PC_1) as a function of distance metrics (linear and upslope distance) for sediment and tadpoles.

Fig. S1. Relationships among linear distance, upslope distance, and elevation for sampled sites.

Fig. S2. Loading scores for each chemical on principal component 1 (PC_1) for PCAs for sediment and tadpoles .

Fig. S3. Spatial interpolation for principal component 1 scores from PCA for pesticide concentrations in tadpoles during Period 2.

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FIGURE LEGENDS

Fig. 1. Sample site locations (triangles) in Sequoia and Kings Canyon National Parks, CA (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/m^3 for Period 1 and 1.74 pg/m^3 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 ½ 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 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 (heavy line for Period 1; light line for Period 2) are shown with a common slope because the Stage × Period interaction term in all Analysis of Covariance analyses was not significant. Data used are detects only. **A**. α-endosulfan I. **B**. Trans-chlordane (one outlier removed). **C**. Cis-nonachlor. **D**. PCB 187.

Fig. 5. Selected significant relationships between chemical concentrations or principal component 1 and distance metrics in stepwise regressions, all during Period 2. 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 ½ 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 in *P. 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; Tables S4 and S6) and for PC_1 ranged from 17 to 28 (median 24; Table S7). Values shown for significant relationships are r^2/direction of relationship (p value for slope ≠ 0). "ns" indicates not significant. "---" indicates chemical is not in dataset or detection frequency was <30% (Tables S4 and S6).

	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
p,p'-DDE	ns	ns	ns	ns	ns	ns	ns	ns

Trans-chlordane	ns	ns	ns	ns	0.178/-(0.045)	ns	ns	ns
Cis-nonachlor	ns	ns	ns	ns	0.241/-(0.011)	ns	ns	ns
Trans-nonachlor	ns	ns	ns	ns	0.405/-(0.001)	ns	ns	ns
Non-Pesticides								
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	----	----

Figure 1

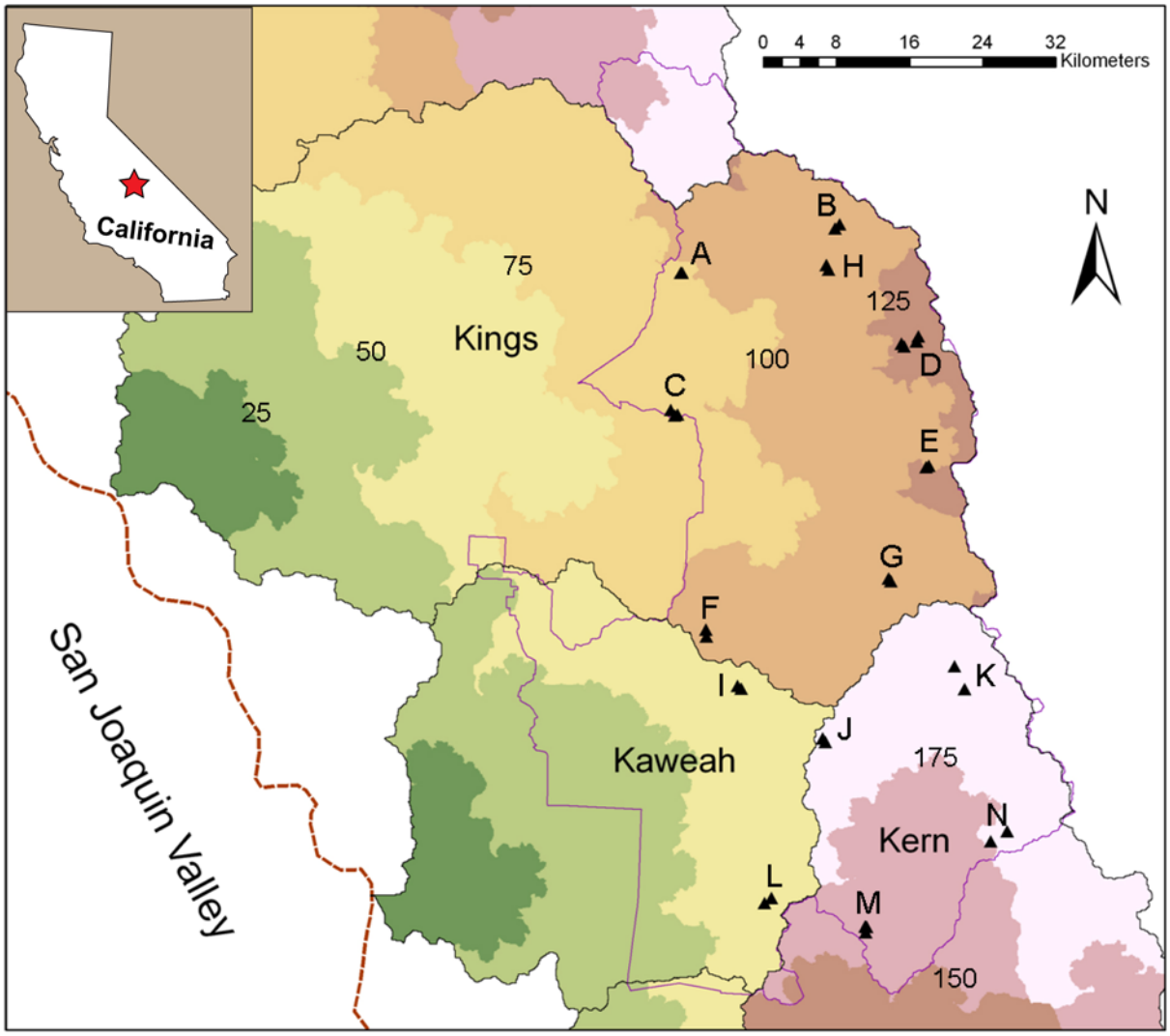

California
0 4 8 16 24 32
Kilometers
N
75
50
25
Kings
100
125
175
150
Kaweah
Kern
San Joaquin Valley
A
B
C
D
E
F
G
H
I
J
K
L
M
N

Figure 2

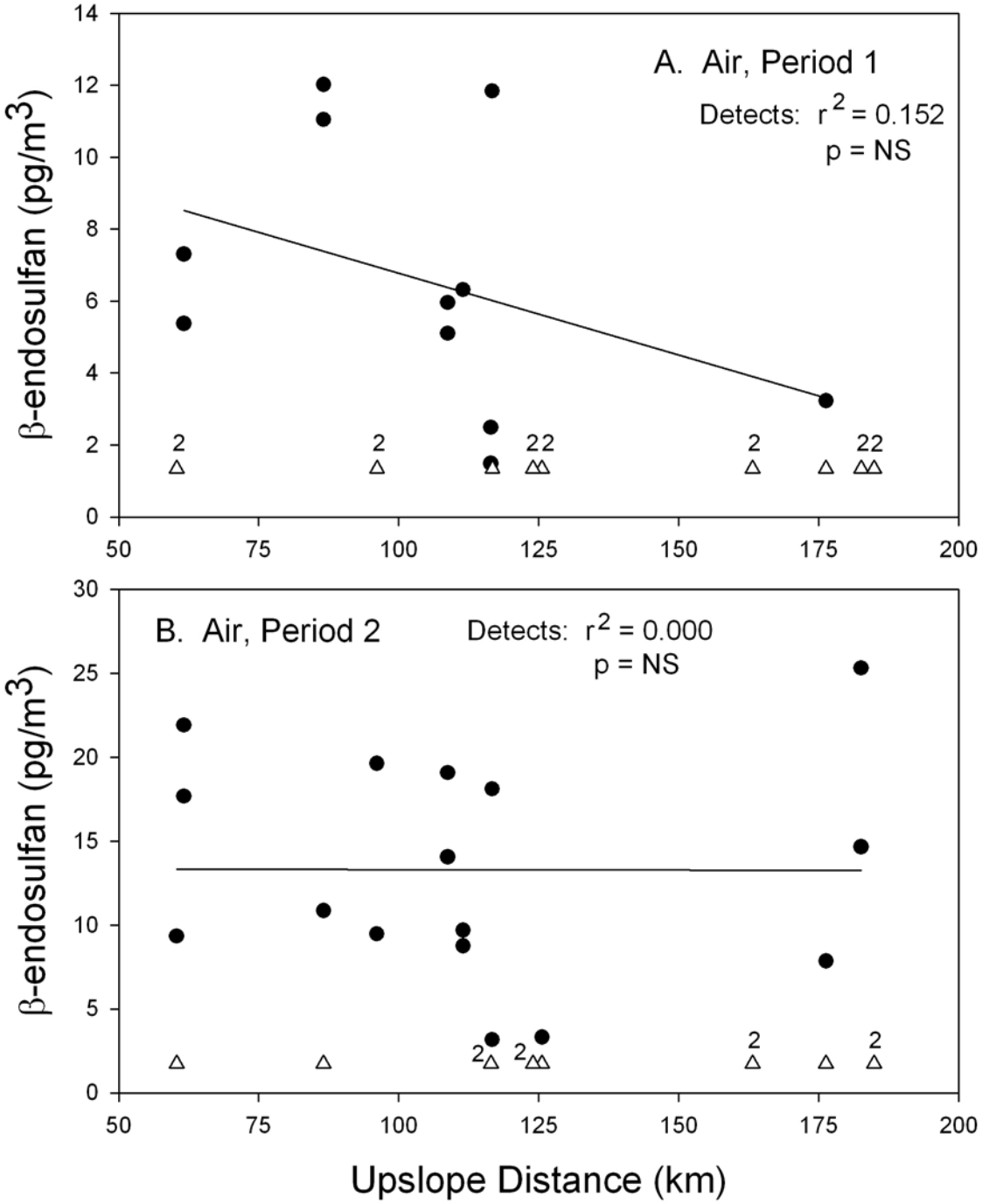

A. Air, Period 1
Detects: r2 = 0.152
p = NS
B. Air, Period 2
Detects: r2 = 0.000
p = NS
β-endosulfan (pg/m3)
Upslope Distance (km)

Figure 3

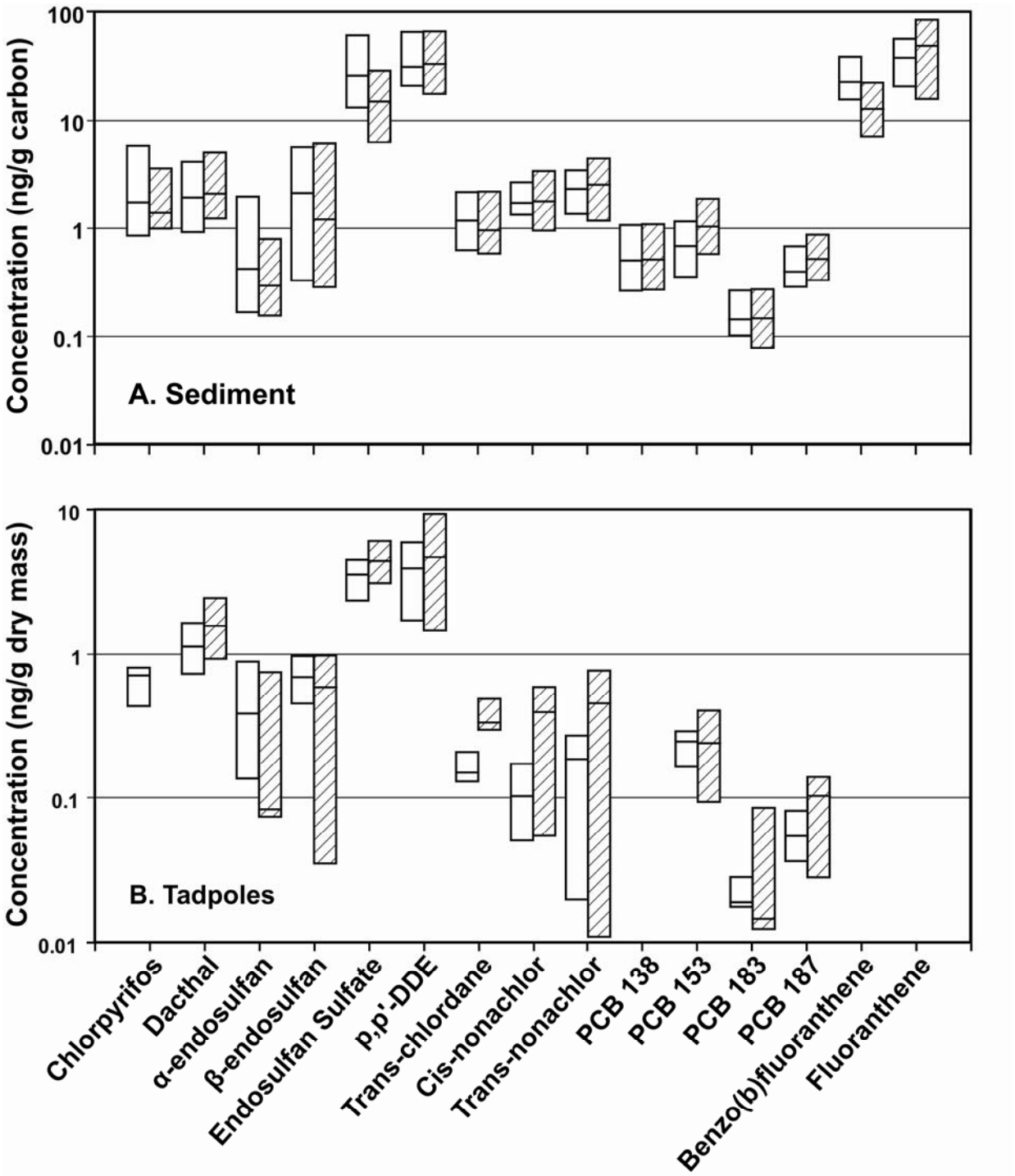

Concentration (ng/g carbon)
100
10
1
0.1
0.01
A. Sediment
Concentration (ng/g dry mass)
10
1
0.1
0.01
B. Tadpoles
Chlorpyrifos
Dacthal
α-endosulfan
β-endosulfan
Endosulfan Sulfate
p,p'-DDE
Trans-chlordane
Cis-nonachlor
Trans-nonachlor
PCB 138
PCB 153
PCB 183
PCB 187
Benzo(b)fluoranthene
Fluoranthene

Figure 4

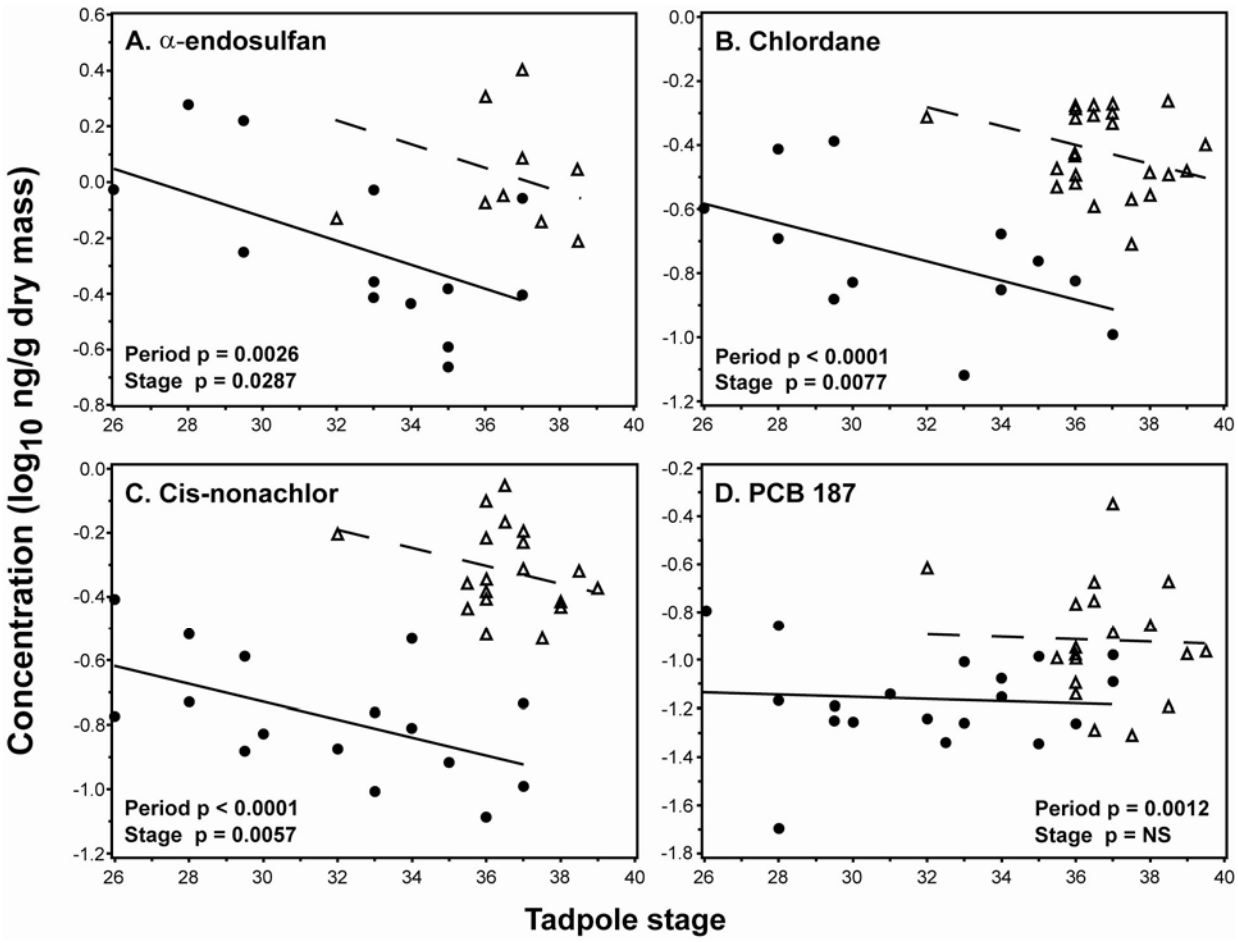

A. α-endosulfan
Period p = 0.0026
Stage p = 0.0287
B. Chlordane
Period p < 0.0001
Stage p = 0.0077
C. Cis-nonachlor
Period p < 0.0001
Stage p = 0.0057
D. PCB 187
Period p = 0.0012
Stage p = NS
Concentration (log10 ng/g dry mass)
Tadpole stage

Figure 5

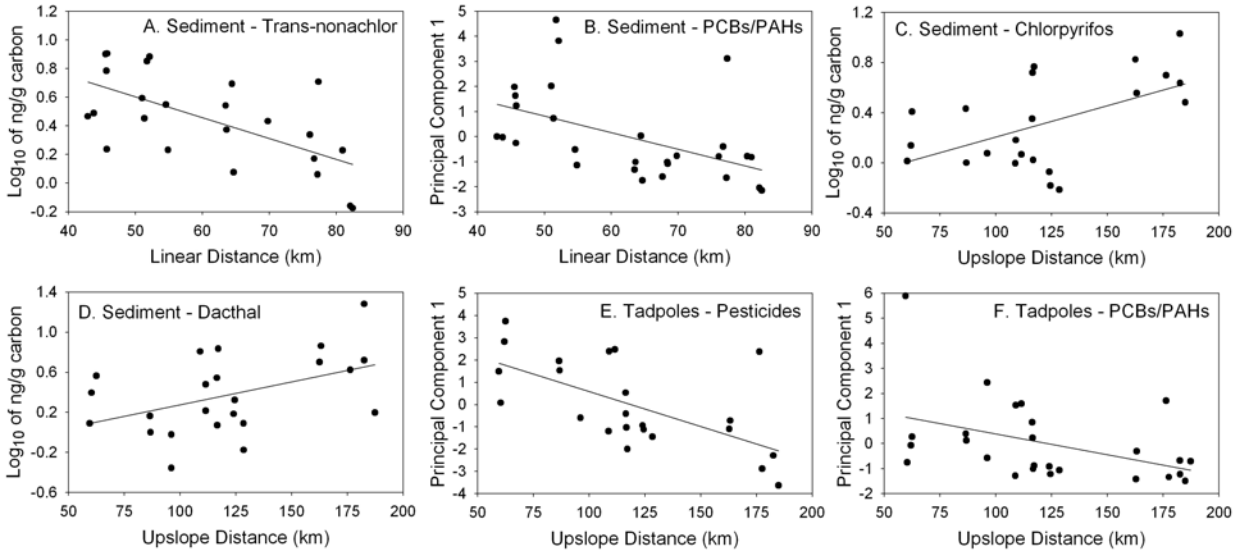
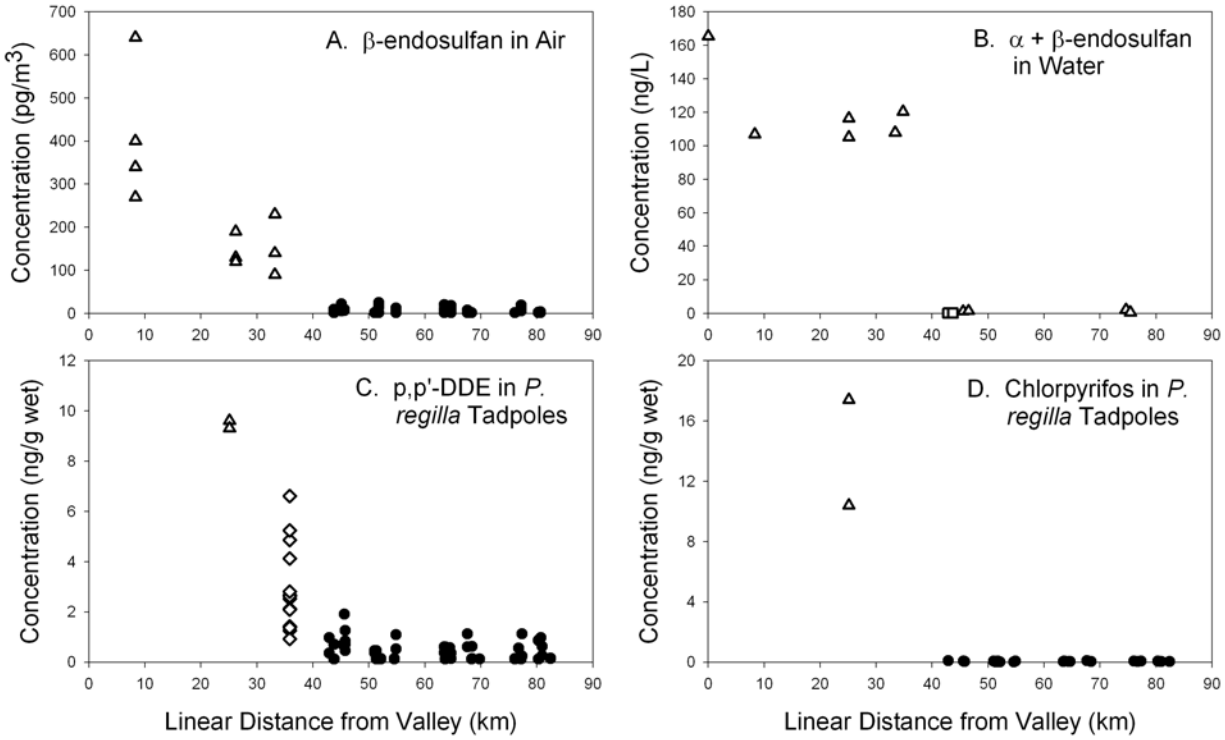

A. Sediment - Trans-nonachlor
Log10 of ng/g carbon
Linear Distance (km)
B. Sediment - PCBs/PAHs
Principal Component 1
Linear Distance (km)
C. Sediment - Chlorpyrifos
Log10 of ng/g carbon
Upslope Distance (km)
D. Sediment - Dacthal
Log10 of ng/g carbon
Upslope Distance (km)
E. Tadpoles - Pesticides
Principal Component 1
Upslope Distance (km)
F. Tadpoles - PCBs/PAHs
Principal Component 1
Upslope Distance (km)

Figure 6


A. β-endosulfan in Air
Concentration (pg/m3)
B. α + β-endosulfan in Water
Concentration (ng/L)
C. p,p'-DDE in P. regilla Tadpoles
Concentration (ng/g wet)
D. Chlorpyrifos in P. regilla Tadpoles
Concentration (ng/g wet)
Linear Distance from Valley (km)
Linear Distance from Valley (km)