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TEMPORAL AND SPATIAL VARIATION OF ATMOSPHERICALLY DEPOSITED ORGANIC CONTAMINANTS AT HIGH ELEVATION IN YOSEMITE NATIONAL PARK, CALIFORNIA, USA

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Abstract − Contaminants used at low elevation, such as pesticides on crops, can be transported tens of kilometers and deposited in adjacent mountains in many parts of the world. Atmospherically deposited organic contaminants in the Sierra Nevada mountains of California, USA, have exceeded some thresholds of concern, but the spatial and temporal distributions of contaminants in the mountains are not well known. We sampled shallow-water sediment and tadpoles (*Pseudacris sierra*) for pesticides, polycyclic aromatic hydrocarbons (PAHs), and polychlorinated biphenyls in four high-elevation sites in Yosemite National Park in the central Sierra Nevada twice during the summers of 2006, 2007, and 2008. Both historic- and current-use pesticides showed a striking pattern of lower concentrations in both sediment and tadpoles in Yosemite than was observed previously in Sequoia-Kings Canyon National Parks in the southern Sierra Nevada. By contrast, PAH concentrations in sediment were generally greater in Yosemite than in Sequoia-Kings Canyon. We suggest that pesticide concentrations tend to be greater in Sequoia-Kings Canyon because of a longer air flow path over agricultural lands for this park along with greater pesticide use near this park. Concentrations for dichlorodiphenyltrichloroethane (DDT)-related compounds in some sediment samples exceeded guidelines or critical thresholds in both parks. A general pattern of difference between Yosemite and Sequoia-Kings Canyon was not evident for total tadpole cholinesterase activity, an indicator of harmful exposure to organophosphorus and carbamate pesticides. Variability of chemical concentrations among sites, between sampling periods within each year, and among years contributed significantly to total variation, although the relative contributions differed between sediment and tadpoles.

Keywords − Cholinesterase, *Pseudacris sierra*, Sediment, Sierra Nevada, Tadpole

INTRODUCTION

Mountain ranges 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 (Day & Wania, also Blais et al. 1998). Particularly vulnerable may be those ranges that lie in close proximity and downwind from areas of high population density, intense agriculture, or intense industrial activity, such as the European Alps, southern slope of the Himalayas, Sierra Nevada of California, and mountains of Costa Rica (Daly and Wania 2005, Daly et al. 2007). The present study focuses on the Sierra Nevada mountain range, which lies adjacent to one of the highest agricultural pesticide-use areas in North America, the Central Valley of California [1]. Even in the remote alpine zone at high elevation (i.e., near or above timberline, > 2750 m), the occurrence of pesticides and other airborne contaminants is well documented [e.g., 2-7], and concern has arisen that airborne contaminants may be having adverse effects on biota at high elevation. For example, concentrations of dichlorodiphenyltrichloroethane (DDT)-related compounds and dieldrin in fish from the southern Sierra Nevada at high elevation exceeded human health thresholds for recreational fishing and/or wildlife health thresholds [8], and dichlorodiphenyldichloroethane (DDE) in lake sediment exceeded guidelines for protection of benthic organisms [7]. However, Bradford et al. [9] concluded there was little evidence for pesticides as the main factor in recent amphibian population declines in the southern Sierra Nevada at high elevation based on lack of correlation between pesticide concentrations and amphibian population status among sites. Despite such concerns, the distributions of airborne contaminants throughout the Sierra Nevada

at high elevation are poorly known except for the southern Sierra Nevada in Sequoia and Kings Canyon National Parks (Fig. 1) where concentrations are generally thought to be greatest [10,11].

Annual variation in contaminant concentrations is also poorly known, which limits comparisons between areas and years. Data for pesticides in the snowpack from a set of western U.S. national parks, including Sequoia National Park, showed that annual variation within sites generally exceeded among-site variation [12]. During other times of the year and in other media, however, temporal and spatial variation in concentrations may differ from the patterns observed in the snowpack. A comparison of annual variation with intra-year and among-site variation would provide important insight into the comparability of previous contaminant measurements at different times and places. The primary objectives of the present study were: (1) to determine whether the contaminant concentrations at high-elevation within Yosemite National Park in the central Sierra Nevada differ from concentrations observed previously in Sequoia-Kings Canyon National Parks in the southern Sierra Nevada [6], and (2) to evaluate annual variation in contaminant concentrations in Yosemite relative to variation within the summer and among sites. We also included in these evaluations total cholinesterase activity (ChE) in tadpoles of the widespread Sierra chorus frog, *Pseudacris sierra* (formerly *P. regilla*). Depression in ChE in this species has been used as a bioindicator of exposure to organophosphorous and carbamate pesticides, many of which are commonly used in the Central Valley [11,13]

MATERIALS AND METHODS

Study sites

The four study sites consisted of four lakes and nearby ponds (2471 - 3206 m elevation) in the east central part of Yosemite National Park (Table 1; Fig. 1). Lakes were separated from each other by 5 to 15 km. The lakes were selected as part of a companion study of the frog *Rana sierrae* to represent high-elevation water bodies that were permanent, ≥ 3 m deep, lacked introduced fish, and could be reached by hiking within one day from a trailhead [14]. All four lakes were considered representative of high elevation lakes in the central Sierra Nevada with respect to size, hydrology, and biota. All lakes had near neutral pH and very low electrical conductivities (data below), which are characteristic for most lakes in the region [15]. Details for site locations and characteristics are provided in Table 1.

Chemical sampling and analysis

Pesticide concentrations were determined in sediment and in whole tadpoles of *Pseudacris sierra*. These media were selected to be comparable to previous sampling in Sequoia-Kings Canyon National Parks (Fig. 1; [6]). Tadpoles of *P. sierra* were selected because this native amphibian is widespread and abundant throughout the Sierra Nevada at high elevation. Water was not sampled because previous sampling in the region showed that the likelihood of detecting pesticides in water was much lower than in sediment [17]. Details for sampling methods, chemical analysis, and estimated detection limits (EDL) are provided elsewhere [6,16], and are summarized here. Sediment was collected with a hand corer at 1.0 m water depth, and the top 2.5 cm of the core was taken as the sample. Tadpoles at Gosner [18] developmental stages 25 to 41 were collected by dip net, placed in plastic bags with lake water,

and transferred to pre-cleaned glass vials. Samples of both sediment and tadpoles were placed on dry ice in the field, and kept frozen until analysis. Samples were collected during two periods during the summers of 2006, 2007, and 2008, with the sampling periods timed to be approximately 30 d apart and the second sampling period occurring prior to the onset of metamorphosis. The dates of sampling for periods 1 and 2 in each year were: 29 July to 2 August and 29 to 31 August, 2006, respectively; 29 June to 1 July and 29 to 31 July, 2007; and 9 to 13 July and 7 to 11 August 2008. Tadpoles were approximately 1 mo old during period 1 and 2 mo old during period 2. Duplicate samples were collected at the same time within a few meters of one another; the frequency of duplicate samples was 10%.

The 69 target analytes were 46 historic- or current-use pesticides or their metabolites, 17 polycyclic aromatic hydrocarbons (PAHs), and 6 polychlorinated biphenyls (PCBs; Table S2 in Supplemental Data). Chemical analyses were conducted in the same laboratory at Oregon State University as used for the previous study in Sequoia and Kings Canyon National Parks [6], and methods previously developed in this laboratory for contaminant analysis in tadpoles and sediment samples were utilized [16,19]. Briefly, tadpole and sediment samples were spiked with isotopically labeled internal standards and analyzed using an Agilent 6890 gas chromatograph / 5973N mass spectrometer in both electron impact and electron capture negative ionization modes. Solvent-based calibration curves were used and instruments were monitored using solvent standards. Analytes were positively identified with a minimum of 3:1 signal to noise ratio, retention time match (± 0.5 minute with the standards), and matching ion ratios (± 20% abundance).

Total organic carbon in sediment was analyzed for 0.2 g dried subsamples using a CNS-2000 Element Analyzer (LECO Corp., St. Joseph, MI, USA). Chemical concentrations in

sediment are reported on a carbon basis (ng/g carbon) because the inorganic content of sediment varied widely among samples and our chemicals of interest partition to the organic component of the sediment. Samples for which associated laboratory blank levels exceeded 33% of the measured chemical concentrations were omitted. Laboratory blanks were processed with each batch of samples (8-12 samples) processed and concentrations reported are blank-subtracted. Water samples collected concomitantly with sediment samples were analyzed for pH and electrical conductivity in the laboratory following methods used in Bradford et al. [20].

A chemical was included in statistical analyses for each medium if the detection frequency among all samples (i.e., all sites, sampling periods, and years) was > 30% and at least half the samples did not have laboratory blank levels > 33% of the measured value. The 30% detection threshold was selected because concentration values less than the EDL were replaced with half the EDL, a technique that yields adequate summary statistics at detection frequency >30% [21]. Values for duplicate samples were averaged except in a few cases where one of the duplicates was not usable due to high blank level, in which case the other duplicate value was used as the site value. Retene was measured but was excluded from analyses because it can originate from both natural and anthropogenic sources [22].

For ChE determination, at each site 18 *P. sierra* tadpoles were collected per time period simultaneously with collection of tadpoles for pesticide analysis. Tadpoles were handled and analyzed as described in Bradford et al. [9]. Tadpoles were individually wrapped and kept frozen on dry ice or at −80^{o}C until analysis. Total cholinesterase was determined through spectrophotometric methods [23] with reagent quantities adjusted for a microplate reader (Synergy model; BioTek, Winooski, VT, USA).

The amount and timing of application of selected pesticides in the San Joaquin Valley (southern arm of Central Valley; Fig. 1) was derived from California Department of Pesticide Regulation Pesticide Use Reports (http://calpip.cdpr.ca.gov/main.cfm).

Statistical analysis

Variability in chemical concentrations, represented by coefficients of variation (*CV*) for detected concentrations, was compared for five types of variation: (1) between duplicate sample pairs, (2) among the four sites, (3) between the two sampling periods, (4) among the three years, and (5) within the entire set of 24 samples (i.e., four sites, three years, twice per year) for each medium. For duplicates, the potential number of sample set-chemical combinations for calculating *CV*s was 48 for sediment (3 sample pairs x 16 chemicals that met the above criteria for statistical analysis) and 27 for tadpoles (3 sample pairs x 9 chemicals that met criteria for statistical analysis; Table S1). Because of many non-detects, however, the realized number of *CV*s was 26 for sediment and 11 for tadpoles. In a similar fashion, the potential number of *CV*s was derived for the other four types of variation (Table S1), and the realized numbers of *CV*s are provided in Fig. 2). Variability among the four sites was represented by six sets of four samples collected within 0 to 3 days of each other (i.e., two times per year for three years). Variability among the two sampling periods was represented by 12 sets of two samples (i.e., each of the four sites each year, for three years). Variability among the three years was represented by 8 sets of 3 samples (i.e., four sites each period, for both periods). Variability among the entire set of 24 samples (i.e., across all sites, periods, and years) was represented by *CV*s for all chemicals. Coefficients of variation were compared among types of variation (e.g., among year versus

198 between duplicates) using non parametric tests because the data were not normally distributed
199 for some sets. The tests were Wilcoxon two-sample tests (2-tailed) when two types were
200 compared and Kruskal-Wallis tests when more than two types were compared.
201 Concentration differences among sites, between sampling periods, and among years were
202 evaluated with Wilcoxon two-sample tests (2-tailed) or Kruskal-Wallis tests because the data
203 were often not normally distributed. For chemicals that showed significant differences, the
204 relative differences within categories were illustrated by normalizing the concentrations relative
205 to the maximum concentrations among the sites, periods, or years. For example, the relative
206 concentration for each chemical-medium combination at a site was calculated by dividing the
207 average concentration at the given site by the maximum of the average concentrations among the
208 four sites. ANOVA was conducted on the normalized concentrations to evaluate the general
209 pattern of difference within each category, and Duncan's multiple range test was used to test for
210 differences among specific sites and years.
211 For comparisons between Yosemite (2006, 2007, or 2008) and Sequoia-Kings Canyon
212 (2005), a chemical was included if it met the 30% detection threshold for either park-year
213 combination in the comparison. Differences in concentrations between the two parks were
214 evaluated using the Wilcoxon 2-sample test (2-tailed) because the data were often not normally
215 distributed. Data for Sequoia-Kings Canyon are from 28 sites sampled twice in 2005;
216 concentrations are from Bradford et al. [6], except for benzo(a)anthracene, benzo(a)pyrene,
217 chrysene+triphenylene, fluorene, and methoxychlor in sediment (unpublished data).
218 To represent ChE for each site-period-year combination, the median value was used for
219 descriptive statistics, whereas the mean of $\log_{10}$-transformed values was used to test for
220 association between ChE and pesticide concentrations (Pearson correlation). Analysis of

variance was used to test the hypothesis that ChE differs among sites, periods, and years. We used a general linear model (GLM) with least-square means option for multiple comparison of means. Split-plot analysis of variance was used to test the significance of differences among sites, and the "t" statistic was used for multiple comparisons of means. The model was:

Model $Log_{10}ChE = Site\ \ Year(Site)\ \ Period\ \ Year\ \ Site \times Period\ \ Year \times Period$

To test differences in ChE between Yosemite (YOSE; 2006, 2007, 2008) and Sequoia-Kings Canyon (SEKI; 2005), GLM with split-plot analysis of variance was conducted. This analysis was run for three comparisons (YOSE 2006 vs. SEKI 2005, YOSE 2007 vs. SEKI 2005, YOSE 2008 vs. SEKI 2005). The model was:

Model $Log_{10}ChE = Park\ \ Site(Park)\ \ Period\ \ Period \times Park$

For both models ChE was log_{10}-transformed and three outliers were removed to achieve normality (Shapiro-Wilk test, $p \geq 0.05$). The models did not include tadpole developmental stage as a variable because in Yosemite a stage effect was not evident in a GLM for ChE as a function of stage alone, or as a function of site, period, year, and stage ($p = 0.1596$ and 0.5887, respectively), and the effect of stage in Sequoia-Kings Canyon was not significant for one period and was minimal for the other [9].

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

244 evaluate the significance of each individual combination. Statistical analyses were performed
245 using SAS® 9.1.3 (SAS Institute Inc., Cary, NC, USA).
246
247 RESULTS AND DISCUSSION
248
249 *Chemicals detected*
250
251 Of the 69 chemicals analyzed in sediment and *P. sierra* tadpoles, 27 were detected in at
252 least one sample (Table S2 in Supplemental Data). These chemicals represent pesticides (11 in
253 sediment, 9 in tadpoles), PAHs (11 in sediment, 2 in tadpoles), and PCBs (5 in sediment, 4 in
254 tadpoles). Eighteen of these (16 in sediment, 9 in tadpoles) met the criteria for further analysis
255 (Fig.3). These were four historic-use pesticide compounds (3 in sediment, 4 in tadpoles), five
256 current-use pesticide compounds (4 in sediment, 4 in tadpoles), five PAHs (5 in sediment, none
257 in tadpoles), and five PCBs (4 in sediment, 1 in tadpoles). Median concentrations for most
258 compounds were on the order of 10 ng/g carbon or less (1 ng/g dry weight [DW]) in sediment
259 and on the order of 1 ng/g DW or less in tadpoles (Fig.3, Tables S2 and S3 in Supplemental
260 Data). In sediment, the predominant pesticide compounds found (i.e., p,p'-DDE, *trans*-
261 chlordane, *cis*- and *trans*-nonachlor, chlorpyrifos, dacthal, α- and β-endosulfan, and endosulfan
262 sulfate) were also the predominant compounds found in Yosemite lake sediments in a previous
263 study [7]. The pH of water bodies sampled was near neutral throughout the study, and electrical
264 conductivity was very low (maximum 17 µS/cm; Table 1).
265 In general, concentrations for historic-use pesticides, PAHs, and PCBs on a dry weight
266 basis (Table S3 in Supplemental Data) were below sediment quality guidelines for freshwater

ecosystems [24]. However, six of 24 samples exceeded the threshold effect concentration for p,p'-DDE (3.2 ng/g DW), which is the concentration below which harmful effects are unlikely to be observed. Also, 1 of 24 samples exceeded the threshold effect concentration for p,p'-dichlorodiphenyldichloroethane (DDD; 4.9 ng/g DW) and the probable effect concentration (28.0 ng/g DW), which is the concentration above which harmful effects are likely to be observed. Among the current-use pesticides, concentrations in *P. sierra* tadpoles for chlorpyrifos and the three endosulfan compounds were many orders of magnitude lower than the tissue concentrations known to be toxic for this species [13].

Variability in Chemical Concentrations

For the 16 focal chemicals in sediment and nine in tadpoles, variability between duplicates was low in comparison to variability among all samples (Fig. 2). For sediment, median *CV* values were 18.8% for duplicates and 60.2% for all samples, representing a factor of 3.2. For tadpoles, median *CV* values were 11.7% for duplicates and 68.1% for all samples, representing a factor of 5.8. The *CV*s for duplicates of sediment and tadpoles were similar to *CV*s representing analytical variability, for the methods utilized, from spike and recovery experiments published in [16] and [19]. *CV*s representing analytical variability for the chemicals that were included in analyses in the present study ranged from 5.1 to 17.2 % in sediment [19] and from 3.5 to 14.6 % in tadpoles [16].

For the three sources of variability that contribute to total variability (i.e., among sites, between periods, among years), the pattern of variability differed between sediment and tadpoles (Fig. 2). First, for tadpoles, the variability for all three sources was significantly greater than

290 duplicate variability, indicating that all sources contribute substantially to overall variation. For
291 sediment, however, only among-site and among-year variability was significantly greater than
292 duplicate variability, whereas between-period variability was not. This difference between
293 tadpoles and sediment suggests that for tadpoles, but perhaps not for sediment, samples collected
294 at multiple sites or years should be collected at similar phenological times (e.g., tadpole
295 developmental stage) in order to be comparable. Second, for tadpoles, amount of variability did
296 not differ significantly among the three sources of variation, whereas for sediment, differences
297 among the three sources were significant (Kruskal-Wallis tests). Indeed, in pairwise
298 comparisons, among-site variability for sediment significantly exceeded among-year variability,
299 and among-year variability significantly exceeded between-period variability (Wilcoxon tests).
300 These findings suggest that future efforts to characterize contaminant concentrations in the Sierra
301 Nevada should include both spatial and temporal (multi-year) components in the sampling
302 design.

303 For both sediment and tadpoles, among-year variability did not significantly exceed
304 among-site variability, a finding that contrasts with pesticides in snowpack at the end of winter at
305 national parks in western North American, including Sequoia National Park in the southern
306 Sierra Nevada [12]. This finding may result from at least three differences between summer and
307 winter conditions. First, transformation rates for contaminants are presumably much greater
308 during summer than winter due to temperature effects and interaction with media and biota, and
309 such degradation undoubtedly varies spatially due to differing environmental conditions among
310 sites. Second, snowpack samples collected at the end of winter represent integration of chemical
311 input over many months, whereas summertime samples may reflect conditions over much shorter
312 time intervals. Third, although contaminant inputs are primarily regional during both summer

and winter [5,25], contaminant inputs likely vary spatially more during summer than winter due to the more localized wind patterns during summer (e.g., up-valley winds; [25]) than the widely circulating cyclonic storms during winter.

The relatively high among-site variability in sediment in comparison to tadpoles may be due to large differences in sediment composition among sites. For example, sediment composition differed conspicuously between McGee Lake (fine grained with much organic content) and Skelton Lake (sandy with little organic content; Table 1). Although chemical concentrations were standardized on a carbon basis, average total organic carbon in sediment varied among the sites by a factor of 10 (Table 1), and differences in sediment characteristics other than carbon content presumably influence chemical concentrations in sediment. Despite the greater among-site variability for sediment relative to tadpoles, sediment has the advantage as a medium to survey for atmospherically deposited organic contaminants in the Sierra Nevada by having lower temporal variability within the summer, more chemicals detected and, unlike tadpoles, it is available year-round.

Concentration differences among sites

Of the 25 chemical-medium combinations in the analysis, concentrations of seven differed significantly among the four sites (Kruskal-Wallis tests). These were three pesticide compounds and three PCBs in sediment, and p,p'-DDE in tadpoles (Fig. 4). In all cases the average concentrations were highest in McGee Lake. As a general pattern, the relative concentrations for the seven chemical-medium combinations collectively differed significantly among sites (ANOVA, $n = 28$, $p < 0.0001$), with the values at McGee Lake significantly greater

than the other three sites, and the other three sites not significantly different from each other (Duncan's multiple range test; Fig. 4).

It is not obvious why McGee Lake would have higher contaminant concentrations than the other three lakes. The finding that six of the seven chemicals that differed among the lakes were from sediment suggests that sediment characteristics primarily account for the differences among sites. Sediment at McGee Lake was conspicuously finer grained with higher total organic carbon content than sediment at the other three sites (Table 1), although concentrations were standardized on a carbon basis. Elevation may be a factor (2471 m for McGee Lake, 3018 to 3206 m for other sites), as Mast et al. [7] found a significant negative correlation between elevation and total pesticide concentrations in sediment (both dry weight and carbon bases) and endosulfan sulfate in water among Yosemite National Park lakes. The magnitude of the elevation effect in their study was similar to the magnitude of differences observed as a function of elevation among lakes in the present study. Another possible explanation is distance from the San Joaquin Valley (90 km for McGee Lake, 100–102 km for other sites; Table 1). However, the magnitude of this difference is small relative to the range for which a distance effect on contaminant concentrations has been demonstrated in the Sierra Nevada [3,6,26].

Concentration differences among sampling periods and years

Chemical concentrations differed significantly between the two sampling periods for six of nine chemicals in tadpoles, and one of 16 in sediment. In all cases, concentrations were greater during period 2 than period 1. Significant chemicals in tadpoles were four historic-use pesticide compounds (*trans*-chlordane, p,p'-DDE, *cis*-nonachlor, *trans*-nonachlor), one current-

359 use pesticide (dacthal [chlorthal dimethyl]), and PCB 187. The significant chemical for sediment
360 was PCB 138. The mean concentrations of the six chemicals in tadpoles during period 1 ranged
361 from 26 to 35% of the mean concentrations during Period 2; for PCB 138 in sediment the
362 corresponding value was 80%.

363 These findings are similar to those made in the southern Sierra Nevada in 2005 in which
364 concentrations for a number of contaminants, primarily in tadpoles, were generally greater
365 during period 2 than period 1 [6]. In both the previous and present study, the cause for the
366 generally greater concentrations in period 2 than period 1 is not clear. In the 2005 study, the
367 concentration differences in tadpoles between sampling periods were independent of tadpole
368 developmental stage, which is largely determined by tadpole age [6]. Moreover, for two current-
369 use pesticides, correspondence between the timing of pesticide application in the San Joaquin
370 Valley (i.e., a likely source for current-use pesticides [25]) and concentrations in the mountains
371 was equivocal. In the present study, correspondence between the timing of dacthal application in
372 the San Joaquin Valley and concentrations in tadpoles in the study sites was also equivocal. In
373 2006 and 2008 dacthal application showed a pattern of increasing use over the 3-month period
374 ending during our sampling period 2, consistent with the pattern of increasing dacthal
375 concentrations in tadpoles. However, in 2007 dacthal application did not increase over the 3-
376 month period, yet dacthal concentrations were generally greater for period 2 as in the other years.

377 Concentrations for nine chemical-medium combinations differed significantly among the
378 three years (Kruskal-Wallis tests). For sediment, these were current-use pesticide compounds
379 (α- and β-endsosulfan, endosulfan sulfate), a historic-use pesticide (*cis*-nonachlor), and PAHs
380 (benzo[a]anthracene, benzo[b]flouranthene, chrysene+triphenylene, fluorene). For tadpoles,
381 these were current-use pesticide compounds (α-endosulfan, β-endosulfan, and endosulfan

sulfate). The general pattern for these differences among years was for concentrations to be lower in 2006 than in 2007 and 2008 (Fig. S1 in Supplemental Data). Specifically, the relative concentrations for the nine chemical-medium combinations collectively differed significantly among years (ANOVA, $n = 27$, $p = 0.0191$), with values in 2006 significantly less than values in the other two years and the other two years not significantly different from each other (Duncan's multiple range test; Fig. S1). Given the diversity of chemicals that differed in concentration among years, it is unclear why 2006 would tend to differ from the other two years. For the current-use pesticide, endosulfan, concentrations among years did not correspond with endosulfan application in the San Joaquin Valley. Indeed, the year with greatest concentrations (2007) was the year with approximately half the application amount during the summer months (June-August) as for the other two years.

Concentration differences between Yosemite and Sequoia-Kings Canyon National Parks

A total of 80 combinations of chemical-medium-year met the criteria for comparing concentrations in Yosemite in 2006, 2007, and 2008 with concentrations in Sequoia-Kings Canyon in 2005. Concentrations differed significantly between the parks in 43 (54%) of the 80 tests (Fig. 5).

Both historic- and current-use pesticides showed a striking pattern of greater concentrations in Sequoia-Kings Canyon than in Yosemite. For historic-use pesticides 12 of 25 chemical-medium-year tests differed significantly between the parks, and concentrations for all of these were greater in Sequoia-Kings Canyon than in Yosemite (Fig. 5). Likewise, for current-use pesticides 20 of 29 comparisons were significant, and all 20 had greater concentrations in

405 Sequoia-Kings Canyon. Ten pesticide compounds were represented in the comparisons: five
406 representing historic-use pesticides (*trans*-chlordane, p,p'-DDE, methoxychlor, *cis*-nonachlor,
407 *trans*-nonachlor) and five representing current-use pesticides (chlorpyrifos, dacthal, α-
408 endosulfan, β-endosulfan, endosulfan sulfate). Among these only p,p'-DDE and methoxychlor
409 did not differ significantly between the parks for at least one comparison.

410 In contrast to the pattern for pesticides, PAHs showed a general pattern of greater
411 concentrations in Yosemite than in Sequoia-Kings Canyon (Fig. 5). PAHs differed significantly
412 between the parks for seven of 14 comparisons, and concentrations for six of these were greater
413 in Yosemite than in Sequoia-Kings Canyon. Six PAHs were represented among the 14 tests, all
414 of which were in sediment: benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene,
415 chrysene+triphenylene, fluoranthene, and fluorene. The PAHs that were significant in at least
416 one test were benzo(a)anthracene, benzo(b)fluoranthene, chrysene+triphenylene, and fluorene.

417 Comparisons for PCBs suggested a pattern of greater concentrations in Sequoia-Kings
418 Canyon than in Yosemite (Fig. 5). However, only four of 12 comparisons were significant, and
419 these were found only in sediment in the comparisons for Yosemite in 2006. The PCBs
420 represented in the 12 tests were PCB 138, 153, 183, and 187, all of which were significant in one
421 test.

422 The pattern of greater pesticide concentrations in Sequoia-Kings Canyon in 2005 than in
423 Yosemite in 2006 to 2008 is consistent with the hypothesis that pesticide concentrations are
424 generally greater in the southern Sierra Nevada than in the central and northern parts of this
425 range [10,11]. This apparent difference between the parks may result from differences in the
426 general pattern of air flow to the parks and differences in the proximity of pesticide use to the
427 parks. For both parks the primary surface air flow path for most of the year is for air to enter the

San Joaquin Valley through the San Francisco Bay area, then move southeast through the Valley before entering the Sierra Nevada (Fig. 1, [25,27]). Land use throughout the San Joaquin Valley is primarily agriculture with extensive pesticide application (California Department of Pesticide Regulation, Pesticide Use Reports; http://calpip.cdpr.ca.gov/main.cfm). Because Sequoia-Kings Canyon lies south of Yosemite, the portion of the air flow pathway that crosses agricultural land is over twice as long for Sequoia-Kings Canyon as it is for Yosemite (see Fig. 1 in [28]). Moreover, pesticide application in the San Joaquin Valley is generally greater near Sequoia-Kings Canyon than near Yosemite (see Fig. 1 in [28].

It is also possible, however, that the differences in pesticide concentrations between the two parks could be explained by differences among years or site locations. For example, application of the current-use pesticides (chlorpyrifos, dacthal, endosulfan) in the San Joaquin Valley during June - August was greater in 2005 than in 2006, 2007, and 2008 in all cases except for dacthal in 2006. This compares with the finding that the concentration of at least one compound representing each of these pesticides was significantly greater in sediment or tadpoles in Sequoia-Kings Canyon in 2005 than in Yosemite in 2006, 2007, and 2008 (i.e., nine pesticide-year combinations). Differences in pesticide application among years, however, cannot explain differences in concentrations of historic-use pesticides between the parks because these pesticides are no longer applied. Weather differences between years were not an obvious factor because the precipitation and average temperature for the year ending in August 2005 in Sequoia-Kings Canyon were similar to the long term averages (i.e., < 0.2 standard deviation from mean), and precipitation and average temperature for the years ending in August 2006, 2007, and 2008 in Yosemite either bracketed the long term average (precipitation) or were within 0.4 standard deviation of the mean (average temperature; based on monthly records for

Lodgepole, Sequoia National Park, 2055 m elevation, and South Entrance Yosemite National park, 1561 m elevation).

An additional possible explanation for the difference in pesticide concentrations between the parks is that the Yosemite sites are further from the source of pesticides in the San Joaquin Valley (90 to 102 km) than the sites represented in Sequoia-Kings Canyon (43–82 km). However, a general pattern of decline in pesticide concentrations with distance from the San Joaquin Valley was not found among the high elevation sites over the 43 – 82 km distance range in Sequoia-Kings Canyon [6].

The generally greater concentrations of PAHs in Yosemite than in Sequoia-Kings Canyon is the reverse of the pattern for pesticides. This suggests that the two parks differ in the sources or transport processes for pesticides and PAHs. Sources of PAHs are primarily from combustion of organic fuels, both anthropogenic (e.g., power plants, internal combustion engines) and natural (e.g., forest fires; [29]). Although both parks are remote from major anthropogenic sources, a difference in vehicular traffic between the parks may account for the differences in PAH concentrations. Vehicular traffic in Yosemite National Park was approximately double that for Sequoia-Kings Canyon National Parks for each year, 2005 to 2008 (National Park Service Monthly Public Use Report, www.nature.nps.gov/stats; A. Esperanza, pers. comm.). Moreover, the Yosemite sites average 4 km from the nearest major road (Highway 120) within the park whereas sites in Sequoia-Kings Canyon average approximately 23 km from the nearest highways (Highways 180, 198) in the parks (Fig. 1). Alternatively, PAH concentrations may have been greater in Yosemite than Sequoia/Kings Canyon because the Yosemite sites lie closer than Sequoia/Kings Canyon sites to the major upwind metropolitan areas around the San Francisco Bay (approximately 210 and 300 km, respectively). Differences

in PAH concentratons between the two parks may also have resulted from in biomass burning in the mountains. Wildfires and control burns occur every year at lower elevations in the vicinity of both parks.

Cholinesterase activity

Total cholinesterase activity (ChE) in *P. sierra* tadpoles varied considerably within and among sites and times (Fig. 6). The coefficient of variation for individual samples within a site at a given time averaged 24.5% (median 22.7%, $n = 22$ site-time combinations), which is similar to the average *CV* observed for *P. sierra* tadpoles in Sequoia-Kings Canyon (18.1% and 26.5% for periods 1 and 2 in 2005, respectively [9]). Among site-time combinations in Yosemite, the median ChE for a combination varied several fold from 0.345 to 1.450 µmol g^{-1} min^{-1}, and averaged 0.615 µmol g^{-1} min^{-1} ($n = 22$). The overall *CV* among median ChE for all site-time combinations was 41.1% ($n = 22$). Coefficients of variation among sites, between periods, and among years were less than this value and were generally similar to each other. Specifically, the median *CV* among sites was 21.9% ($n = 6$ combinations), between periods was 23.1% ($n = 10$ combinations), and among years was 28.6% ($n = 8$ combinations).

Comparisons in ChE among sites, periods, and years showed that the time of sampling is an important determinant of ChE (Fig. 6). Differences in ChE were significant between periods ($p < 0.0001$) and among years ($p < 0.0001$), but not among sites (general linear model equation 1). Total cholinesterase was greater in period 2 (average of site medians, 0.710 µmol g^{-1} min^{-1}) than in period 1(0.520 µmol g^{-1} min^{-1}). The developmental stage of tadpoles was generally

497 greater for period 2 (average stage 35.9) than period 1 (average 31.7), but no relationship was
498 found between stage and ChE (see Methods and Materials). For ChE among years, post hoc tests
499 showed that ChE differed significantly among all years, with the greatest difference between
500 2008 (average of medians, 0.860 µmol g^{-1} min^{-1}) and the other two years (0.536 and 0.469 µmol
501 g^{-1} min^{-1} in 2006 and 2007, respectively).

502 No relationship was found between ChE and concentrations of the only pesticide detected
503 with ChE depressing capability, i.e., the current-use organophosphate, chlorpyrifos. Comparison
504 between chlorpyrifos concentrations and ChE was limited, however, because chlorpyrifos was
505 detected in only seven samples in sediment and two in tadpoles. Correlation analyses for the
506 seven detected samples in sediment (Pearson correlation), and for all 22 samples in sediment
507 (Spearman rank test), were not significant (p = 0.1 and 0.6, respectively). Even if the sample
508 size had been larger, though, depression of ChE in *P. sierra* tadpoles would not be expected at
509 the chlorpyrifos concentrations observed in tadpoles in the present study (maximum 2.4 ng/g
510 DW; Table S2 in Supplemental Data) or in Sequoia-Kings Canyon in 2005 (maximum 1.4 n/g
511 [6]). Based on data from Sparling and Fellers [13], these authors argued that such concentrations
512 are several orders of magnitude lower than those demonstrated to substantially depress ChE in *P.*
513 *sierra*.

514 A general pattern of difference in ChE between Yosemite and Sequoia-Kings Canyon
515 was not evident. Total ChE activity did not differ between Yosemite in 2006 or 2007 and
516 Sequoia-Kings Canyon in 2005 (general linear model equation 2). By contrast, ChE in Yosemite
517 in 2008 (average site median = 0.615 µmol g^{-1} min^{-1}) was significantly greater than ChE in
518 Sequoia-Kings Canyon in 2005 (0.525 µmol g^{-1} min^{-1}, $p < 0.0001$). This difference, however,
519 may represent a time effect, rather than a space effect, because ChE for Yosemite in 2008 was

also greater than for Yosemite in 2006 and 2007 (see above), and was strongly influenced by the exceptionally high ChE level at one site in Yosemite during period 2 in 2008 (Fig. 6). Thus, regardless of the greater concentrations observed for chlorpyrifos and other pesticides in Sequoia-Kings Canyon than in Yosemite, this difference has apparently not been sufficient to depress tadpole cholinesterase levels in Sequoia-Kings Canyon relative to Yosemite...

CONCLUSION

A challenge in characterizing chemical contamination is to distinguish patterns in space and time (signal) from variability (noise). This challenge can be minimized when the variability is known and the intensity of sampling can be adjusted to correspond with the variability. In the case of airborne chemicals in the Sierra Nevada, future efforts to characterize contamination should consider sampling at many sites, over multiple years, and at multiple times during the year, because the present study showed that variation in each of these components can be substantial. Moreover, the relative magnitudes of these three types of variation differed among the two media, i.e., sediment and tadpoles.

While little sampling has been conducted throughout the Sierra Nevada as a whole, results from the present study at high elevations supports the notion that the southern Sierra has the greatest exposure to many airborne pollutants. Although concentrations for most pollutants were low (e.g, parts per billion range in sediment on dry weight basis), concentrations for some historic-use DDT-related compounds have exceeded guidelines or critical thresholds in both Yosemite and Sequoia-Kings Canyon National Parks.

SUPPLEMENTAL DATA

Table S1. Number of sample set-chemical combinations for calculating coefficients of variation (*CV*) for five types of variation: between duplicates, among sites, between sampling periods, among years, and among all samples.

Table S2. Detection frequency and concentrations of chemicals found in sediment (carbon basis) and *Pseudacris sierra* tadpoles (dry weight basis) in Yosemite National Park, California.

Table S3. Detection frequency and concentrations of chemicals found in sediment (dry weight basis) in Yosemite National Park, California.

Fig. S1. Relative concentrations of nine chemical/medium combinations whose concentrations differed significantly among the three years.

Supplemental Data References

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567
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655

656 Table 1. Characteristics of sites in Yosemite National Park sampled for organic contaminants[a]

Site Name	McGee Lake	Conness Pond	Tioga Pond	Skelton Lake
Latitude	37.902°	37.971°	37.908°	37.932°
Longitude	−119.430°	−119.345°	−119.258°	−119.305 °
Elevation (m)	2471	3176	3018	3206
Distance to San Joaquin Valley (km)	90.0	100.2	101.8	100.2
Maximum Depth (m)	4	3	4	11
Lake Area (ha)	2.2	0.4	0.8	4.7
pH, mean (range)	6.7 (6.2-7.0)	6.8 (6.6-6.9)	7.1 (6.8-7.4)	6.8 (6.6-6.9)
Conductivity, µS/cm, mean (range)	6.1 (4.4-8.9)	4.7 (3.1-6.1)	14.5 (11.9-17.2)	4.6 (3.7-5.2)
Sediment Carbon Content, g carbon/g DW (range)	0.215 (0.191-0.246)	0.079 (0.047-0.122)	0.123 0.027-0.183)	0.022 (0.013-0.032)

657 [a] Sediment was sampled in the designated water bodies. Tadpoles were collected in the water
658 body or adjacent ponds, except for Skelton Lake, where tadpoles were sampled at the nearest
659 location that contained the species, a pond 3.1 km southwest (37.908 °, -119.326°; 2957 m
660 elevation). All lakes were underlain by granitic rock.

661

662 FIGURE CAPTIONS

663

664 Figure 1. Location of sites sampled in Yosemite National Park (present study) and
665 Sequoia and Kings Canyon National Parks [6,9]. Roads shown are the major ones entering the
666 parks. Elevations above 2400 m within the Sierra Nevada are depicted by the tan colored
667 polygons.

668 Figure 2. Coefficients of variation (*CV*s) for chemical concentrations (detects only) for
669 five types of variability in sediment and tadpoles: between duplicate samples, among sites,
670 between sampling periods, among years, and among all samples. Data shown are median
671 (horizontal line) and interquartile range (i.e., 25 to 75 percentiles). Number of *CV*s in each
672 variability group is shown above each box. Asterisks indicate group *CV*s that are significantly
673 different from duplicate *CV*s (Wilcoxon 2-sample test, 2-tailed).

674 Figure 3. Concentrations of chemicals in *Pseudacris sierra* tadpoles (top) and sediment
675 (bottom) that met criteria for further analysis. Values below estimated detection limits (EDL)
676 were replaced with half of the EDL. Data shown are median (horizontal line) and interquartile
677 range (i.e., 25 to 75 percentiles). Sample sizes (13 to 24) and detection frequencies (30 to 100%)
678 are provided in Table S2 in Supplemental Data.

679 Figure 4. Relative concentrations of seven chemical-medium combinations whose
680 concentrations differed significantly among the four sites. The relative concentration for each
681 chemical-medium combination and site was calculated by dividing the average concentration at a
682 given site by the maximum of the average concentrations among the four sites. The value for

683 McGee Lake was 1.0 for all chemical-medium combinations because this site had the maximum
684 average concentration in all cases.

685 Figure 5. Relative concentrations of chemicals between Yosemite National Park (YOSE)
686 in 2006, 2007, and 2008 (present study) and Sequoia-Kings Canyon National Parks (SEKI) in
687 2005 [6]. Values are calculated as: (mean concentration in YOSE – mean concentration in
688 SEKI) / (maximum of mean concentrations for YOSE and SEKI). Thus, values > 0 indicate
689 concentrations are greater in YOSE, whereas values < 0 indicate concentrations are greater in
690 SEKI. Media represented are sediment (S) and *Pseudacris sierra* tadpoles (T). Values shown
691 represent only the comparisons that differed significantly ($p < 0.05$) between the two areas
692 (Wilcoxon 2-sample test, 2-tailed). Chemicals shown are historic-use pesticides (HUPs): trans-
693 chlordane (circles), cis-nonachlor (squares), trans-nonachlor (triangles); current-use pesticides
694 (CUPs): chlorpyrifos (squares), dacthal (downward triangles), α-endosulfan (circle), β-
695 endosulfan (upward triangles), and endosulfan sulfate (crosses); PAHs: benzo(a)anthracene
696 (circles), benzo(b)fluoranthene (upward triangle), chrysene+triphenylene (squares), and fluorene
697 (downward triangles); PCBs: PCB 138 (circle), 153 (upward triangle), 183 (square), and 187
698 (downward triangle).

699 Figure 6. Total cholinesterase activity for individual tadpoles at each site. Box
700 represents interquartile range (i.e., 25 to 75 percentiles), horizontal line indicates median, vertical
701 lines represent range, and asterisks indicate outliers. Open boxes represent sampling period 1;
702 hatched boxes represent period 2. Sample sizes were approximately 18 at each site, except it was
703 8 for Tioga Pond, 2008, period 2.

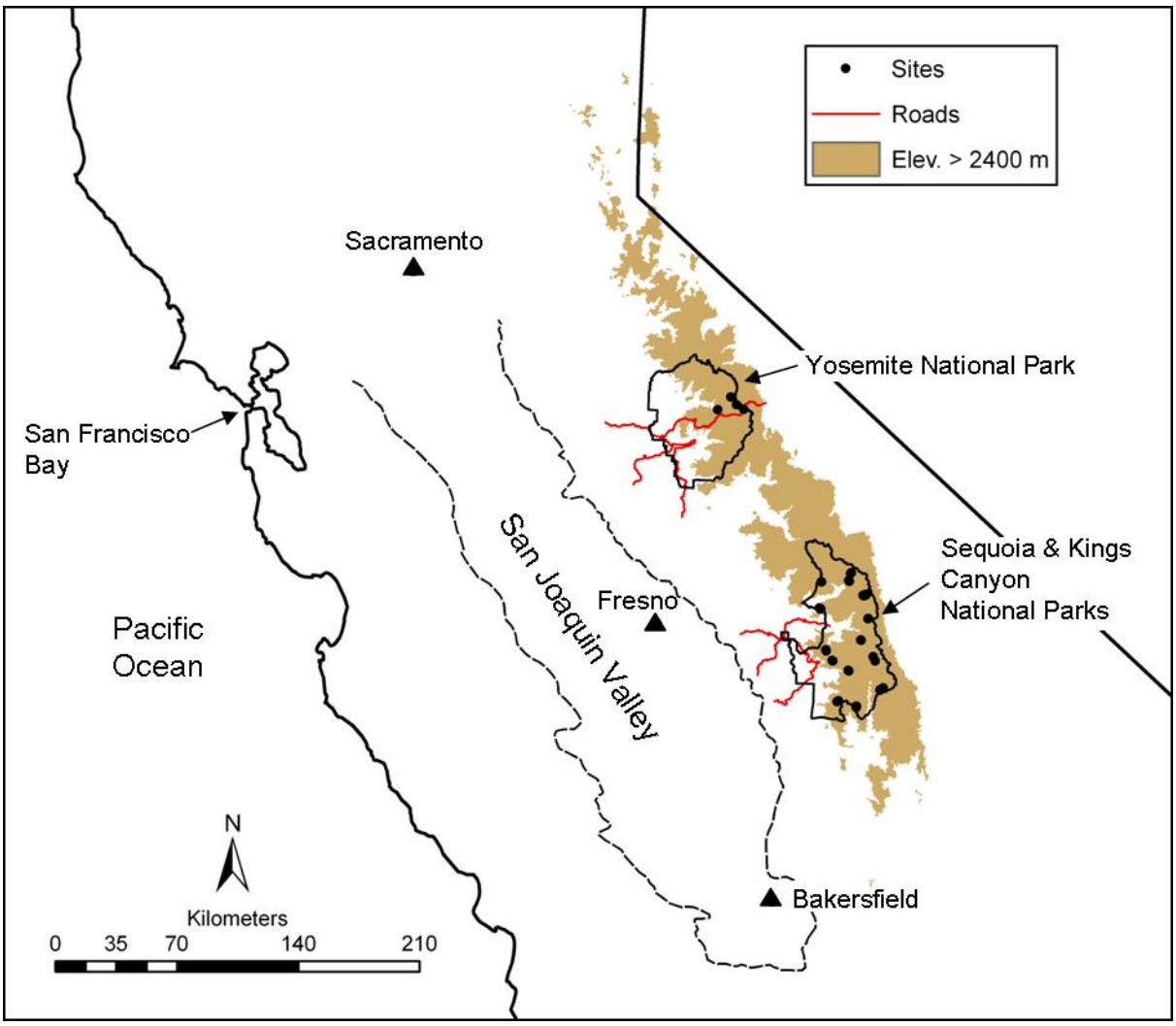
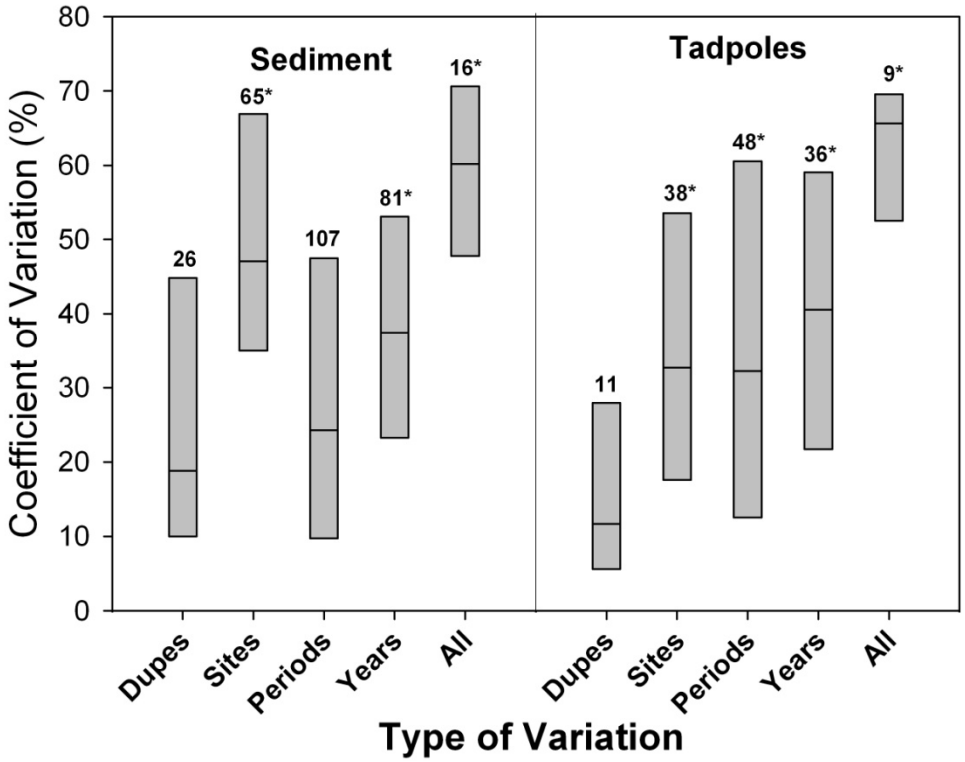
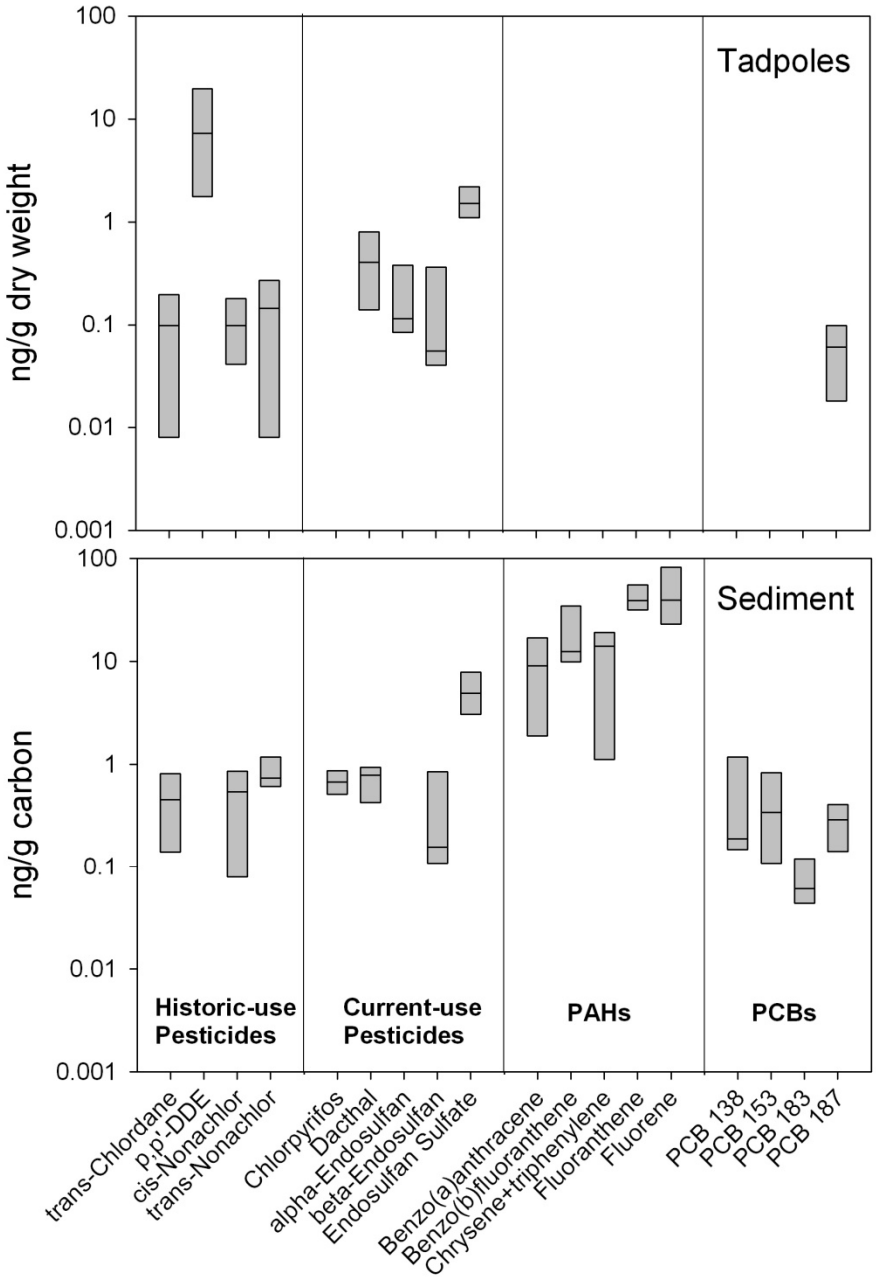

Sites
Roads
Elev. > 2400 m
Sacramento
Yosemite National Park
San Francisco
Bay
San Joaquin Valley
Fresno
Sequoia & Kings
Canyon
National Parks
Pacific
Ocean
N
Kilometers
0 35 70 140 210
Bakersfield

Figure 1



711
712
713 Figure 2

714
715


Tadpoles
Sediment
ng/g dry weight
ng/g carbon
100
10
1
0.1
0.01
0.001
Historic-use Pesticides
Current-use Pesticides
PAHs
PCBs
trans-Chlordane
p,p'-DDE
cis-Nonachlor
trans-Nonachlor
Chlorpyrifos
Dacthal
alpha-Endosulfan
beta-Endosulfan
Endosulfan Sulfate
Benzo(a)anthracene
Benzo(b)fluoranthene
Chrysene+triphenylene
Fluoranthene
Fluorene
PCB 138
PCB 153
PCB 183
PCB 187

716

717 Figure 3

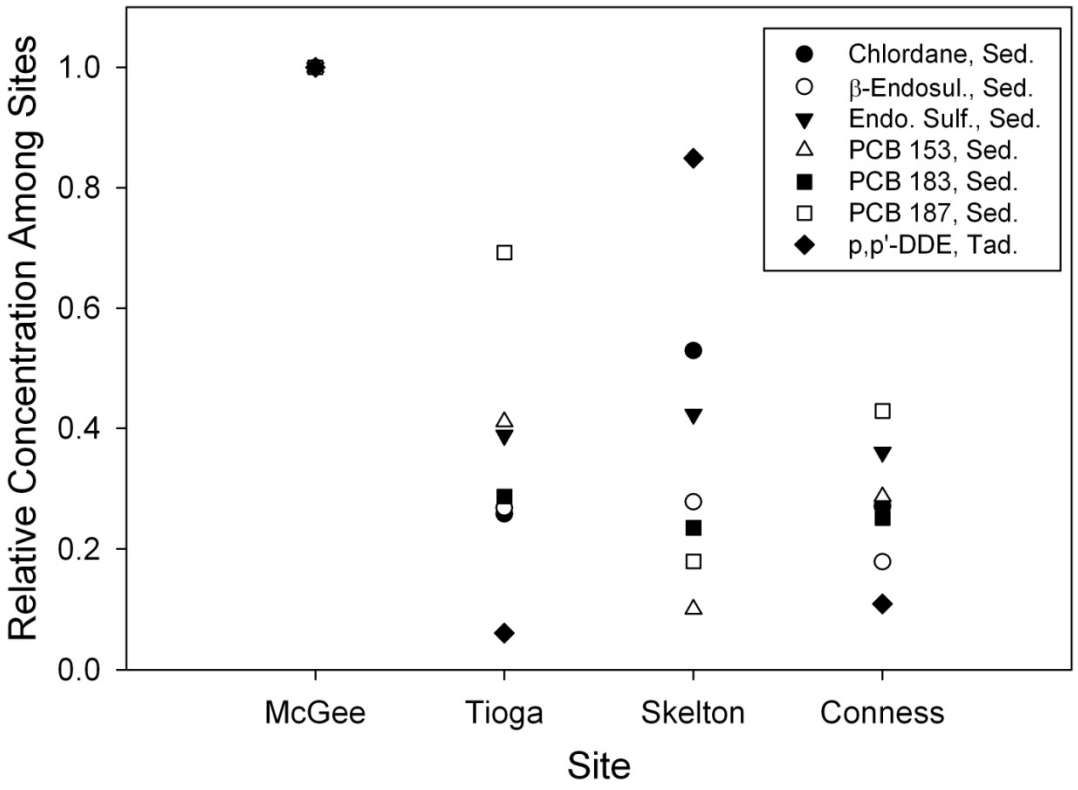

Relative Concentration Among Sites
1.0
0.8
0.6
0.4
0.2
0.0
McGee
Tioga
Skelton
Conness
Site
Chlordane, Sed.
β-Endosul., Sed.
Endo. Sulf., Sed.
PCB 153, Sed.
PCB 183, Sed.
PCB 187, Sed.
p,p'-DDE, Tad.

Figure 4

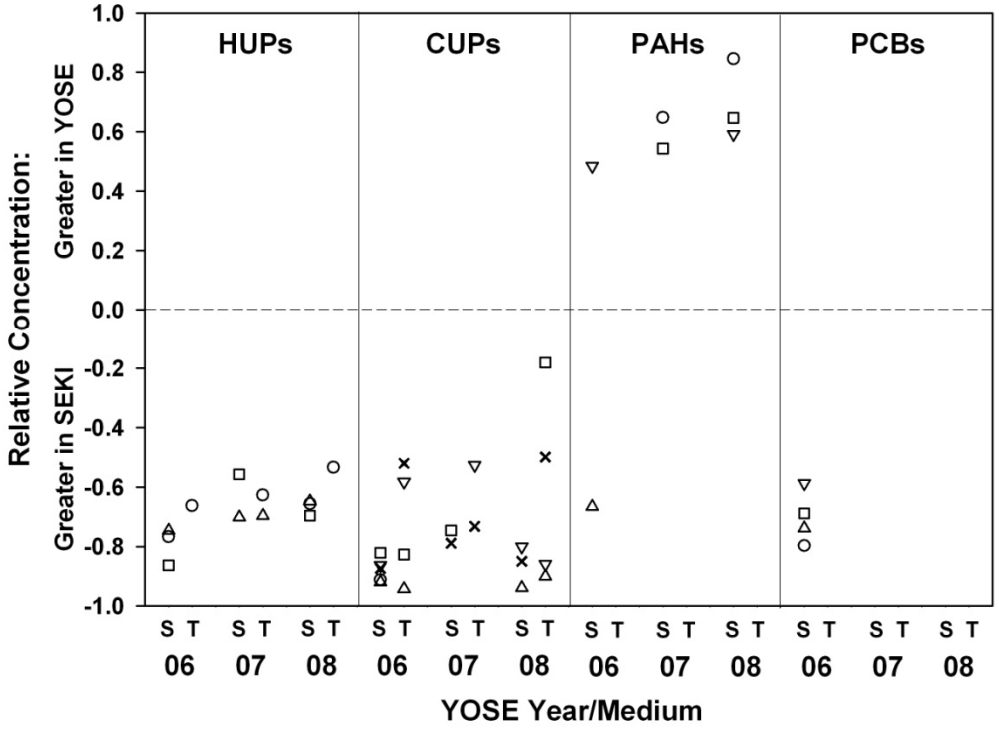

HUPs
CUPs
PAHs
PCBs
Relative Concentration:
Greater in YOSE
Greater in SEKI
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
S T
06
07
08
YOSE Year/Medium

Figure 5

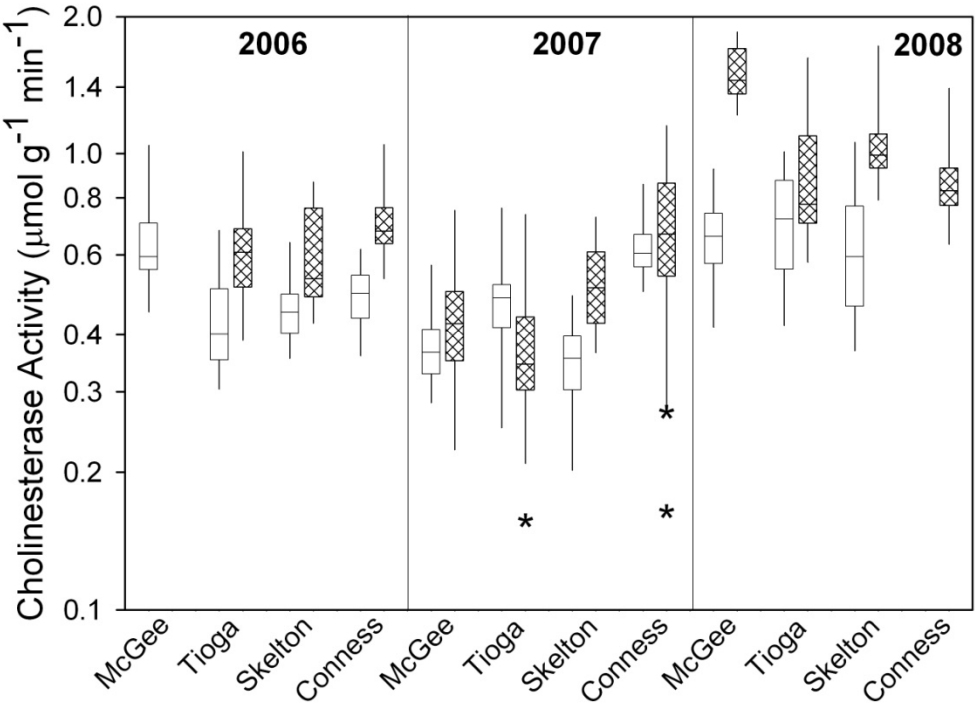

2006
2007
2008
Cholinesterase Activity (µmol g-1 min-1)
2.0
1.4
1.0
0.8
0.6
0.4
0.3
0.2
0.1
McGee
Tioga
Skelton
Conness
McGee
Tioga
Skelton
Conness
McGee
Tioga
Skelton
Conness

Figure 6

SUPPLEMENTAL DATA

Temporal and Spatial Variation of Atmospherically Deposited Organic Contaminants at High Elevation in Yosemite National Park, California, USA

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Table S1. Number of sample set-chemical combinations for calculating coefficients of variation (*CV*) for five types of variation: between duplicates, among sites, between sampling periods, among years, and among all samples. The potential number of combinations represents the number of sets × number of chemicals. The realized number of combinations is less than the potential number due to insufficient frequency of detection for some combinations (see text).

Type	Medium	# Samples in Set	# Sets	# Chemicals	Potential # Set-Chemical Combinations	Realized Set-Chemical Combinations
Duplicates						
	Sediment	2	3	16	48	26
	Tadpoles	2	3	9	27	11
Sites						
	Sediment	4	6	16	96	65
	Tadpoles	4	6	9	54	38
Periods						
	Sediment	2	12	16	192	107
	Tadpoles	2	12	9	108	48
Years						
	Sediment	3	8	16	128	81
	Tadpoles	3	8	9	72	36
All						
	Sediment	24	1	16	16	16
	Tadpoles	24	1	9	9	9

Table S2. Detection frequency and concentrations of chemicals found in sediment (carbon basis) and *Pseudacris sierra* tadpoles (dry weight basis) in Yosemite National Park, California. Values are from four sites sampled twice during the summers of 2006, 2007, and 2008. "Usable samples" refers to those in which laboratory blank levels did not exceed 33% of measured value. Values below the estimated detection limit (EDL) have been substituted with 1/2 EDL. Estimated detection limits for chemicals are provided for sediment in Bradford et al. [1] and for tadpoles in Stanley et al. [2]. "P25" and "P75" refer to 25th and 75th percentiles, respectively. NA indicates not applicable. Forty two chemicals were not detected in any sample.[1]

Chemical	Usable Samples	Detected Samples	Detection Frequency (%)	Median	P25	P75	Min	Max
SEDIMENT (ng/g carbon)								
Historic-use Pesticides								
trans-Chlordane	24	18	75.0%	0.455	0.140	0.807	0.009	1.707
p,p'-DDD	24	1	4.2%	9.583	7.780	11.922	3.285	80.803
p,p'-DDE	24	7	29.2%	11.437	8.284	53.667	4.748	206.819
Methoxychlor	19	5	26.3%	12.210	9.905	26.671	3.424	60.849
cis-Nonachlor	24	17	70.8%	0.541	0.079	0.859	0.029	2.231
trans-Nonachlor	24	23	95.8%	0.739	0.608	1.174	0.053	1.530
Current-use Pesticides								
Chlorpyrifos	23	7	30.4%	0.671	0.514	0.863	0.200	5.111
Dacthal	24	23	95.8%	0.783	0.426	0.936	0.019	3.635
α-Endosulfan	24	7	29.2%	0.208	0.167	0.273	0.064	1.109
β-Endosulfan	24	10	41.7%	0.157	0.109	0.850	0.058	1.934
Endosulfan Sulfate	24	24	100.0%	4.907	3.069	7.829	0.820	16.709
PAHs								
Benzo(a)anthracene	22	13	59.1%	9.037	1.889	16.953	0.562	101.780
Benzo(a)pyrene	24	3	12.5%	3.987	3.311	5.183	1.233	53.997
Benzo(b)fluoranthene	24	8	33.3%	12.479	9.822	34.621	3.438	139.226
Benzo(e)pyrene	24	3	12.5%	13.499	11.779	17.438	4.418	62.615
Benzo(ghi)perylene	24	1	4.2%	1.807	1.569	2.249	0.620	58.072
Benzo(k)fluoranthene	24	1	4.2%	5.207	4.519	6.478	1.785	17.849

Chrysene+triphenylene	24	15	62.5%	13.993	1.111	19.146	0.327	50.653
Fluoranthene	24	24	100.0%	39.017	31.712	55.037	10.537	229.816
Fluorene	23	20	87.0%	39.442	22.965	81.851	8.707	102.176
Phenanthrene	7	7	100.0%	228.309	164.941	254.827	156.977	264.622
Retene	19	18	94.7%	216.584	79.945	10648.534	18.328	15781.554
PCBs								
PCB 118	15	3	20.0%	0.126	0.108	0.173	0.061	3.553
PCB 138	16	6	37.5%	0.188	0.148	1.181	0.055	2.800
PCB 153	16	8	50.0%	0.342	0.109	0.827	0.053	1.912
PCB 183	16	7	43.8%	0.060	0.044	0.120	0.023	0.341
PCB 187	17	15	88.2%	0.288	0.143	0.408	0.016	0.956
TADPOLES (ng/g dry weight)								
Historic-use Pesticides								
trans-Chlordane	23	14	60.9%	0.099	0.008	0.195	0.005	0.579
p,p'-DDE	23	13	56.5%	7.199	1.756	19.603	0.960	50.308
cis-Nonachlor	23	12	52.2%	0.099	0.041	0.180	0.026	0.540
trans-Nonachlor	23	14	60.9%	0.144	0.008	0.270	0.005	0.965
Current-use Pesticides								
Chlorpyrifos	15	2	13.3%	0.147	0.109	0.293	0.096	2.434
Dacthal	23	18	78.3%	0.404	0.140	0.798	0.052	2.152
alpha-Endosulfan	23	8	34.8%	0.115	0.083	0.377	0.069	0.575
beta-Endosulfan	23	8	34.8%	0.055	0.040	0.364	0.033	0.636
Endosulfan Sulfate	23	23	100.0%	1.501	1.099	2.194	0.662	4.669
PAHs								
Fluoranthene	22	3	13.6%	0.661	0.583	0.899	0.467	14.595
Retene	23	11	47.8%	7.111	2.773	55.192	2.047	1117.054
PCBs								
PCB 118	12	2	16.7%	0.122	0.106	0.168	0.090	0.258
PCB 153	18	3	16.7%	0.131	0.096	0.253	0.074	0.387
PCB 183	20	1	5.0%	0.015	0.014	0.020	0.010	0.057

PCB 187	15	8	53.3%	0.060	0.018	0.099	0.014	0.309

[1] Chemicals not detected in any sample were: Pesticides – Acetochlor, Alachlor, Aldrin, Atrazine, Chlordane (cis and oxy), Cyanazine, o,p'-DDD, o,p'-DDE, o,p'-DDT, p,p'-DDT, Diazinon, Dieldrin, Endrin, Endrin aldehyde, Ethion, Etridiazole, Hexachlorocyclohexane (alpha, beta, delta, and gamma), Heptachlor, Heptachlor epoxide, Hexachlorobenzene, Malathion, Methyl parathion, Metolachlor, Metribuzin, Mirex, Parathion, Prometon, Propachlor, Simazine, Triallate, Trifluralin; PAHs - Acenaphthene, Acenaphthylene, Anthracene, Dibenz(a,h)anthracene, Indeno(1,2,3-cd)-pyrene, Pyrene; PCBs - PCB 101.

Table S3. Detection frequency and concentrations of chemicals found in sediment (dry weight basis) in Yosemite National Park, California. Information same as in Table S2except concentrations below are ng/g dry weight instead of ng/g carbon.

Chemical	Usable Samples	Detected Samples	Detection Frequency (%)	Median	P25	P75	Min	Max
SEDIMENT (ng/g DW)								
Historic-use Pesticides								
trans-Chlordane	24	18	75.0%	0.039	0.008	0.128	0.000	0.326
p,p'-DDD	24	1	4.2%	0.682	NA	NA	NA	NA
p,p'-DDE	24	7	29.2%	0.748	0.294	12.083	0.154	39.509
Methoxychlor	19	5	26.3%	1.822	0.305	3.420	0.161	9.898
cis-Nonachlor	24	17	70.8%	0.039	0.009	0.095	0.001	0.426
trans-Nonachlor	24	23	95.8%	0.078	0.022	0.139	0.001	0.270
Current-use Pesticides								
Chlorpyrifos	23	7	30.4%	0.048	0.018	0.143	0.009	0.779
Dacthal	24	23	95.8%	0.075	0.013	0.147	0.001	0.666
α-Endosulfan	24	7	29.2%	0.015	0.006	0.038	0.004	0.203
β-Endosulfan	24	10	41.7%	0.014	0.004	0.120	0.003	0.429
Endosulfan Sulfate	24	24	100.0%	0.375	0.115	1.536	0.019	3.269
PAHs								
Benzo(a)anthracene	22	13	59.1%	0.420	0.112	2.206	0.036	8.630
Benzo(a)pyrene	24	3	12.5%	0.419	NA	NA	0.058	6.570
Benzo(b)fluoranthene	24	8	33.3%	1.873	0.311	3.261	0.162	11.804
Benzo(e)pyrene	24	3	12.5%	1.265	NA	NA	0.208	6.396
Benzo(ghi)perylene	24	1	4.2%	0.129	NA	NA	NA	NA
Benzo(k)fluoranthene	24	1	4.2%	0.371	NA	NA	NA	NA
Chrysene+triphenylene	24	15	62.5%	0.409	0.100	3.504	0.021	5.771
Fluoranthene	24	24	100.0%	3.878	1.104	9.507	0.499	19.485
Fluorene	23	20	87.0%	2.702	1.318	9.690	0.223	22.930

Phenanthrene	7	7	100.0%	21.606	5.320	43.615	3.969	63.097
Retene	19	18	94.7%	14.771	3.751	2034.222	1.098	3762.993
PCBs								
PCB 118	15	3	20.0%	0.008	NA	NA	0.003	0.248
PCB 138	16	6	37.5%	0.017	0.005	0.114	0.004	0.535
PCB 153	16	8	50.0%	0.021	0.003	0.118	0.002	0.365
PCB 183	16	7	43.8%	0.004	0.001	0.017	0.001	0.065
PCB 187	17	15	88.2%	0.036	0.006	0.058	0.000	0.183

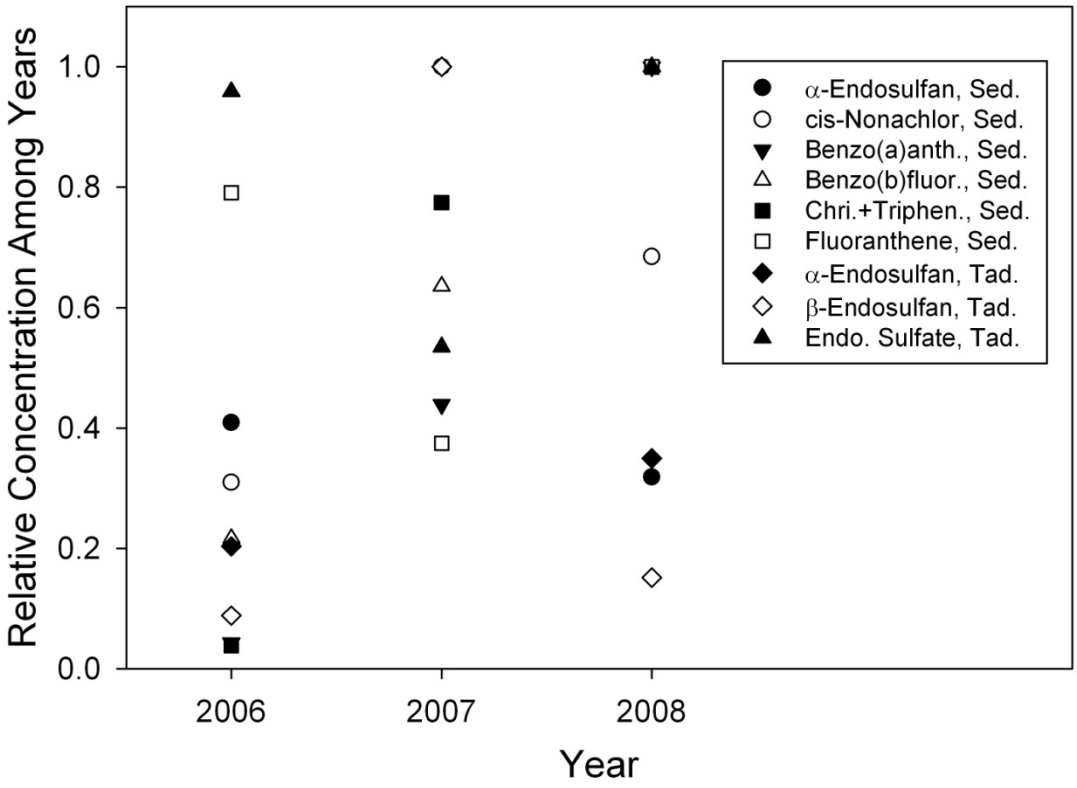

Figure S1. Relative concentrations of nine chemical/medium combinations whose concentrations differed significantly among the three years. The relative concentration for each chemical/medium combination and year was calculated by dividing the average concentration for the given year by the maximum of the average concentrations among the three years.

SUPPLEMENTAL DATA REFERENCES

1. Bradford DF, Stanley K, McConnell LL, Tallent-Halsell NG, Nash MS, Simonich SM. 2010. Spatial patterns of atmospherically deposited organic contaminants at high-elevation in the southern Sierra Nevada mountains, California. *Environ Toxicol Chem* 29:1056-1066.

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