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

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David F. Bradford[1], Kerri Stanley[2], Laura L. McConnell[3], Nita G. Tallent-Halsell[1], Maliha S. Nash[1], and Staci M. Simonich[4,6]

[1]U.S. Environmental Protection Agency, National Exposure Research Laboratory, Landscape Ecology Branch, Las Vegas, Nevada, [2]Department of Environmental and Molecular Toxicology, Oregon State University, Corvallis, OR,
[3]U. S. Department of Agriculture, Agricultural Research Service, Environmental Management and Biproduct Utilization Laboratory, Beltsville, MD, [4]Department of Chemistry, Oregon State University, Corvallis, OR

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 the 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 likewise similar among sites. A general relationship for concentrations at high elevation 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.

Introduction

Airborne agricultural pesticides and other contaminants are being transported many tens of kilometers to remote locations in mountain areas, and they have been implicated as a cause for dramatic population declines of several amphibian species, and adverse effects on fish [1,2]. One of the strongest cases is for frogs (*Rana* spp.) at high elevation of the Sierra Nevada of California [3]. Evidence for this pesticide effect, however, relies primarily on correlations between frog population status and a metric for amount of upwind pesticide use that assumes pesticide concentrations decrease with distance from source areas up to 150 km away. Some evidence exists for a decrease with distance from the edge of the Central Valley up to a few tens of kilometers within the mountains [4]. However, the habitat for these frogs lies primarily at high elevation many tens of kilometers from the edge of the Valley, and the magnitude and temporal variation of pesticide concentrations in this environment have been largely unmeasured.

Objective

The present study tested the hypothesis that atmospherically deposited pesticides and other semi-volatile organic contaminants at high elevation in the Sierra Nevada indeed decrease in concentration with distance from the Central Valley. The goal was to evaluate the generality of resulting patterns with distance across many chemicals, multiple media, and multiple times. We then compared our findings with previous studies closer to the Central Valley to evaluate the general pattern of concentrations from the Central Valley to the crest of the mountains. The study was conducted in the southern Sierra Nevada, which is adjacent to the San Joaquin Valley (southern arm of Central Valley), because airborne contaminant concentrations are generally greatest in the southern Sierra and this area has been subjected to a number of previous studies concerning amphibian populations and air pollution.

Methods

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.).

- The study area was Sequoia and Kings Canyon National Parks, California, at high elevation (2785 – 3375 m; 43 – 82 km from San Joaquin Valley; Fig. 1).
- Twenty-eight water bodies (e.g., Fig. 2) were sampled in 14 dispersed areas (A to N in Fig. 1).
- Media sampled were air, sediment, and tadpoles of a non-declining, abundant frog, Pseudacris sierra. Air was sampled by passive air samplers for 30 d (Fig. 3).
- Samples were collected twice during summer of 2005 (Periods 1 and 2).
- Target analytes for sediment and tadpoles were 46-48 pesticides or their metabolites, 17 PAHs, and 6-7 PCBs. Target analytes for air were 22 pesticides and 5 polybrominated diphenyl ethers. Estimated detection limits were extremely low [5].
- Distance metrics were (1) linear distance to the closest point on the edge of San Joaquin Valley, and (2) upslope distance, the path water would flow from the sampling site to edge of the valley. Upslope distance was used as a surrogate for the flow path taken by daily upslope winds (mountain winds) typical for the southern Sierra Nevada during summer.
- Principal components analysis (PCA) was conducted for pesticides and PAHs/PCBs separately to derive a metric that represented these chemicals collectively (i.e., principal component 1 [PC_1]).
- Associations between chemicals and distance metrics were evaluated by stepwise regression for 57 combinations of a chemical metric (n ≤ 17), medium (air, sediment, tadpoles), and sampling period (n = 2). Chemical metrics were concentrations of ≤ 15 chemicals and PC_1. Covariates were elevation and, for tadpoles, developmental stage.
- Additional details are provided in Bradford et al. [5].

Results and Discussion

Fig. 2. Examples of sites sampled.

- Chemicals Detected
  - In air, only β-endosulfan was detected more than once. Concentrations were very low, on the order of 10 pg/m3 (Fig. 4).
  - In sediment, 15 chemicals were detected at >30% of sites (median 83%) during at least one sampling period. For tadpoles 12 chemicals were detected at >30% of sites (median 74%). These chemicals included both historic- and current-use pesticides, PCBs, and PAHs (Fig. 5). Concentrations were low, mostly < 10 ng/g carbon in sediment and <1 ng/g dry weight in tadpoles.
  - Concentrations of several chemicals in tadpoles were negatively related to tadpole developmental stage (Fig. 6).
- Composition of Chemical Suites
  - The composition of chemical suites was generally similar among sites. This is shown by principal component analyses (PCA) in which all chemicals loaded positively on principal component 1 (PC_1), and the majority of chemicals in each PCA had similar loading values on PC_1 (Fig. 7).

Results and Discussion (*continued*)

Fig. 3. Media represented was air sampled by polyurethane disk within metal housing, sediment collected from top 2.5 cm at 1 m water depth, and tadpoles of *Pseudacris sierra*.

- Such similarity in chemical composition across sites suggests that chemical transport patterns (e.g., chemical mixtures transported and their temporal variation) have been similar among sites.
- Concentrations at High Elevation versus Distance from the San Joaquin Valley
  - A clear pattern of chemical concentrations with distance from the San Joaquin Valley was not apparent, either as a function of linear and upslope distance or upslope distance. Most analyses showed no relationship with distance, and the few significant relationships were conflicting. Specifically:
    - Air: β-endosulfan concentrations were negatively related to upslope distance during Period 1 (Fig. 4 A)
    - Tadpoles: α-endosulfan concentrations and PC_1 scores for pesticides and PCBs/PAHs were negatively related to upslope distance during Period 2 ([Table 1; Fig. 8 E and F).
    - Sediment: Eight chemicals and PC_1 for PCBs/PAHs were significantly negatively related to linear distance during Period 2 (Table 1; Fig. 8 A and B), whereas one pesticide during Period 1 and three during Period 2 were positively related to upslope distance (Table 1; Fig. 8 C and D).
- General Geographic Pattern Across the Sierra Nevada
  - Our results for pesticides at high elevation can be combined with other studies conducted mostly at low elevation and closer to the San Joaquin Valley to evaluate a Valley-to-crest gradient (Fig. 9).
  - The general pattern was for pesticide concentrations to decrease with distance away from the San Joaquin Valley up to about 40 km, beyond which concentrations were very low and did not decrease appreciably with further distance from the Valley (Fig. 9). Coincidentally, elevation increased up to about 40 km, beyond which elevation remained above 2500 m.

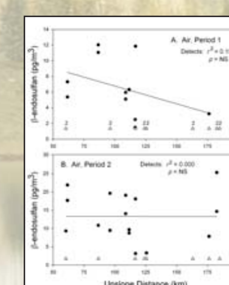

Fig. 4. β-endosulfan concentration in air as a function of upslope distance from the San Joaquin Valley during Periods 1 (A) and 2 (B). Solid circles indicate values above estimated detection limit (EDL); open triangles indicate samples below EDL. Values assigned for samples below EDL are 1.34 pg/m^3 for Period 1 and 1.74 pg/m^3 for Period 2. Regression lines and statistics shown apply to detected values (circles). Non-parametric correlation for all values (detects and nondetects) was significant only for Period 1 (A; Spearman rank test, p = 0.015).

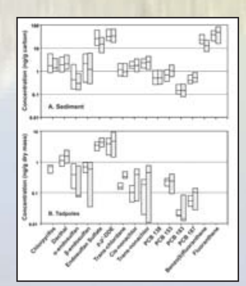

Fig. 5. Chemical concentrations in sediment (A) and tadpoles (B). Values below estimated detection limits (EDL) were replaced with ½ EDL. Data shown are median (horizontal line within box) and 25th and 75th percentiles (box limits). Open boxes indicate Period 1; hatched boxes indicate Period 2.

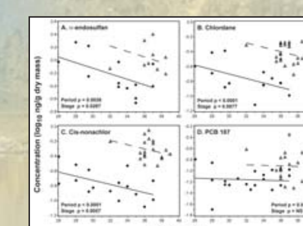

Fig. 6. Chemical concentrations in tadpoles for selected chemicals as a function of tadpole developmental stage during Period 1 (solid circles) and Period 2 (open triangles). Regression lines (solid line for Period 1; dashed line for Period 2) are shown with a common slope because the Stage × Period interaction term in Analysis of Covariance analyses was not significant.

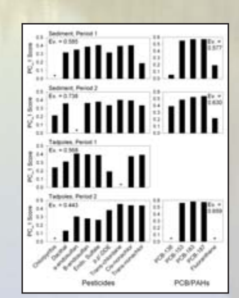

Fig. 7. Loading scores for each chemical on principal component 1 (PC_1) for principal components analysis for sediment and tadpoles. "Ev." indicates eigenvalue for PC_1. "*" indicates chemical omitted from analysis because it was not represented in dataset or many values were missing.

	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	Neg
Chlorpyrifos	ns	Pos	ns	ns	ns	Pos	----	----
Dacthal	ns	ns	ns	ns	ns	Pos	ns	ns
α-endosulfan	ns	ns	ns	ns	----	----	ns	Neg
β-endosulfan	ns	ns	ns	ns	ns	Pos	ns	ns
Endosulfan sulfate	ns	ns	ns	ns	Neg	ns	ns	ns
p,p'-DDE	ns	ns	ns	ns	ns	ns	ns	ns
Trans-chlordane	ns	ns	ns	ns	Neg	ns	ns	ns
Cis-nonachlor	ns	ns	ns	ns	Neg	ns	ns	ns
Trans-nonachlor	ns	ns	ns	ns	Neg	ns	ns	ns
Non-Pesticides								
All PCB/PAHs (PC_1)	ns	ns	----	----	Neg	ns	ns	Neg
PCB 138	ns	ns	----	----	Neg	ns	----	----
PCB 153	ns	ns	ns	ns	Neg	ns	ns	ns
PCB 183	ns	ns	----	----	Neg	ns	ns	ns
PCB 187	ns	ns	ns	ns	Neg	ns	ns	ns
Benzo(b)fluoranthene	ns	ns	----	----	----	----	----	----
Fluoranthene	ns	ns	----	----	ns	ns	----	----

Table 1. Results from stepwise regressions for chemical concentrations and principal component 1 (PC_1) as a function of linear and upslope distance from the San Joaquin Valley for sediment and Pseudacris sierra tadpoles. PC_1 is derived from separate principal component analyses for all pesticides and all polychlorinated biphenyls/polycyclic aromatic hydrocarbons (PCB/PAHs). The direction of significant (p<0.05) relationships is indicated as positive (Pos) or negative (Neg); "ns" indicates not significant; "----" indicates chemical not in dataset or detection frequency was <30%.

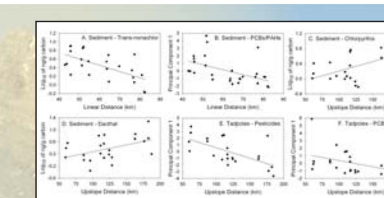

Fig. 8. Selected significant (p<0.05) relationships between chemical concentrations or principal component 1 and distance metrics in stepwise regressions, all during Period 2.

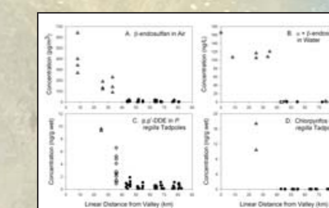

Fig. 9. Concentrations of pesticide compounds as a function of linear distance from the San Joaquin Valley edge within the Kaweah, Kings, and Kern watersheds from this and other studies. Months represented are June through September of various years. Values less than the estimated detection limit (EDL) are shown as ½ EDL. Symbols and data sources as follows. A. Open triangles [4], closed circles (present study). B. Open triangles [4,6], open squares [7], closed circles [8]. C. *P. regilla* [= *Pseudacris sierra*] tadpoles; open triangles [9], open diamonds [10], solid circles (present study). D. *P. regilla* [= *Pseudacris sierra*] tadpoles; open triangles [9], solid circles (present study).

Conclusions

- Within the high-elevation zone, a general relationship for chemical concentrations as a function of distance from the San Joaquin Valley was not evident across chemical, medium, and time.
- By contrast, for the entire gradient from the Valley edge to the Sierra crest, a combination of studies shows that pesticide concentrations generally decrease with distance away from the Valley up to about 40 km, beyond which concentrations remain low and decrease little with further distance from the Valley.
- Thus, support is provided for use of a distance-weighted metric to reflect pesticide exposure up to 40 km from the Valley, but not beyond that.

Literature Cited

1. Ackerman LK, Schwindt AR, Simonich SLM, Koch DC, Blett TF, Schreck CB, Kent ML, Landers DH. 2008. Atmospherically deposited PBDEs, pesticides, PCBs, and PAHs in western U.S. National Park fish: Concentrations and consumption guidelines. *Environ Sci Technol* 42:2334-2341.
2. Sparling DW, Fellers GM, McConnell LL. 2001. Pesticides and amphibian population declines in California, USA. *Environ Toxicol Chem* 20:1591-1595.
3. Davidson C, Knapp RA. 2007. Multiple stressors and amphibian declines: dual impacts of pesticides and fish on yellow-legged frogs. *Ecol Appl* 17:587-597.
4. LeNoir JS, McConnell LL, Fellers GM, Cahill TM, Seiber JN. 1999. Summertime transport of current-use pesticides from California's Central Valley to the Sierra Nevada mountain range, USA. *Environ Toxicol Chem* 18:2715-2722.
5. 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.
6. Fellers GM, McConnell LL, Pratt D, Datta S. 2004. Pesticides in mountain yellow-legged frogs (*Rana muscosa*) from the Sierra Nevada mountains of California, USA. *Environ Toxicol Chem* 23:2170-2177.
7. Landers DH, Simonich SL, Jaffe DA, Geiser LH, Campbell DH, Schwindt AR, Schreck CB, Kent ML, Hafner WD, Taylor HE, Hageman KJ, Usenko S, Ackerman LK, Schrlau JE, Rose NL, Blett TF, Erway MM. 2008. The fate, transport, and ecological impacts of airborne contaminants in western national parks (USA). EPA/600/R-07/138. U.S. Environmental Protection Agency, Corvallis, Oregon, USA.
8. Bradford DF, Heithmar EM, Tallent-Halsell NG, Momplaisir GM, Rosal CG, Varner KE, Nash MS, Riddick LA. 2010. Temporal patterns and sources of atmospherically deposited pesticides in alpine lakes of the Sierra Nevada, California, USA. *Environ Sci Technol* 44:4609-4614.
9. Datta S, Hansen L, McConnell L, Baker J, LeNoir J, Seiber JN. 1998. Pesticides and PCB contaminants in fish and tadpoles from the Kaweah River basin, California. *Bull Environ Contam Toxicol* 60:829-836.
10. Cowman D. 2005. Pesticides and amphibian declines in the Sierra Nevada mountains, California. Ph.D. Thesis. Texas A & M University, College Station, TX, USA.

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For more information contact David F. Bradford at bradford.david@epa.gov.

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