

WET DEPOSITION OF CURRENT-USE PESTICIDES IN THE SIERRA NEVADA  
MOUNTAIN RANGE, CALIFORNIA, USA

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**Abstract**—Atmospheric inputs of pesticides transported from California's Central Valley to the Sierra Nevada mountains (California, USA) were investigated by collecting winter–spring precipitation (rain and snow) from Sequoia National Park and from the Lake Tahoe basin. Pesticides currently used in California's Central Valley were detected in snow and rain samples from two elevations in Sequoia National Park (SNP) in the southern Sierras. At the lower elevation site (533 m), chlorothalonil was present at the highest levels (<0.4–85 ng/L), followed by malathion (<0.046–24 ng/L), diazinon (<0.21–19 ng/L), and chlorpyrifos (1.3–4.4 ng/L). At 1,920 m elevation, chlorothalonil was also present at the highest levels (<0.57–13 ng/L) followed by diazinon (<0.057–14 ng/L), chlorpyrifos (1.1–13 ng/L), and malathion (<0.045–6 ng/L). Trifluralin,  $\alpha$ - and  $\gamma$ -hexachlorocyclohexane (HCH), and  $\alpha$ - and  $\beta$ -endosulfan were also detected at both locations and at lower concentrations, generally ranging from 0.5 to 2 ng/L. In the Lake Tahoe basin, elevation 2,200 m, malathion was also found in snow at concentrations ranging from <0.046 to 18 ng/L, as was diazinon (<0.057–7 ng/L), chlorpyrifos (0.30–3.4 ng/L), and chlorothalonil (0.66–1.7 ng/L). Chlorothalonil, chlorpyrifos,  $\alpha$ - and  $\gamma$ -HCH, and  $\alpha$ -endosulfan were found in surface and deep water samples at two locations in Lake Tahoe and at concentrations similar to those found in snow within the lake basin. Lake Tahoe basin snow samples in general had lower concentrations than those from SNP. This difference in concentration levels reflects the closer proximity of downwind pesticide usage to SNP than the Lake Tahoe basin. An estimated annual loading of one chemical, chlorpyrifos, of 24 to 31 kg/year was made for the SNP land area. Comparisons of observed concentrations were made with reported aquatic toxicity and water criteria levels.

**Keywords**—Pesticide Sierra Nevada Mountains Atmospheric transport Precipitation

## INTRODUCTION

Several reports have documented the atmospheric transport and deposition of pesticides and other trace contaminants far from their points of release. For example,  $\alpha$ - and  $\gamma$ -hexachlorocyclohexane (HCH) and *p,p'*-DDE were measured at  $\mu\text{g}/\text{m}^3$  levels in air near Antarctica [1,2]. Pesticides and polychlorinated biphenyls (PCBs) occur in air and water from the polar regions [3–5] and many other remote locations [6]. Atmospheric transport and deposition processes have been effective in distributing residues of these persistent compounds throughout the global environment [7]. In the cold polar regions, tons of these compounds have become permanently trapped and cycle within the ecosystems of these delicate regions.

Far fewer reports have been made of the less persistent, currently used pesticide residues in remote environments. However, recent measurements by Chernyak et al. [8] in air, fog, and the surface microlayer (top 1 mm of the ocean surface) in the Bering and Chukchi seas resulted in detection of atrazine, chlorothalonil, chlorpyrifos, endosulfan, and trifluralin. We report here that the intrusion of both persistent organochlorine and currently used pesticides in the Sierra Nevada

mountains (California, USA) is pervasive. This study has expanded upon an earlier report from our laboratory that organophosphate pesticides emitted from spraying of dormant orchards in the heavily agriculturalized Central Valley of California are present in air, fogwater, and rain in the valley [9–11] and, in addition, are deposited in wintertime rain at the 2,000 m elevation in Sequoia National Park (SNP) in levels as high as 100 ng/L for diazinon, 10 ng/L for chlorpyrifos, and 10 ng/L for ethyl parathion and its oxon breakdown product [12]. The park lies downwind from proximate San Joaquin Valley, the southern half of California's Central Valley, but wholly within the Sierra Nevada mountain range (Fig. 1). In another recent study, PCBs were found in air, snow, water, and lake trout from Lake Tahoe (California, USA). Comparison of PCB congener patterns in the various media as well as from a nearby comparison lake implicated wet deposition in the form of snow as an important source of PCBs to the Lake Tahoe basin [13], suggesting that Lake Tahoe may be essentially an important receptor for atmospheric inputs to the region.

Deteriorating environmental quality has stimulated interest in the Sierra Nevada mountains as a sink for airborne pollution from human activity in California's valleys and coastal metropolitan areas [14]. Drost and Fellers [15] have raised the hypothesis that a connection exists between deposited pesticide residues and the decline of populations of certain amphibians in the Sierra Nevada mountains. Much earlier Cory et al. [16]

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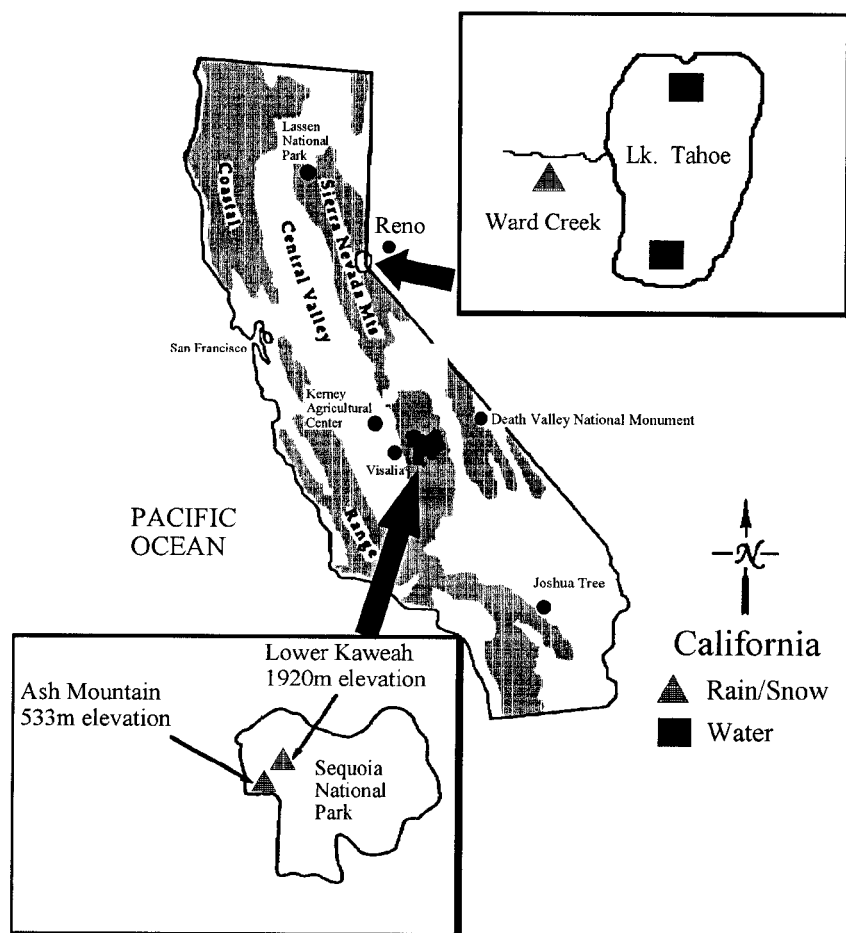


Fig. 1. Map of Lake Tahoe basin and Sequoia National Park, California, USA. Locations of water and wet deposition sampling are designated.

found DDT residues in biota from the Sierra Nevadas. We have recently obtained evidence that PCBs and *p,p'*-DDE are present in surface waters, fish, and frogs at the 500 m elevation in SNP [17].

This project was designed as a preliminary investigation into the magnitude of wet deposition loadings of currently used pesticides to the Sierra Nevada mountains. We report here the analysis of rain and snow from winter and spring storms from the Lake Tahoe basin and three locations in the SNP region, as well as surface and deeper water from Lake Tahoe. The wet deposition concentrations are compared with detailed pesticide use data from California's Central Valley, and estimates of wet and dry atmospheric deposition loadings to SNP for chlorpyrifos are presented.

#### MATERIALS AND METHODS

##### Water

Lake Tahoe surface water was collected on June 20 and 21, 1995. Water samples at Lake Tahoe (9–17 L) were collected at two stations (Fig. 1) from the research vessel *John LeConte* operated by the University of California–Davis Tahoe Research Group. At the southern lake station (38°59.25'N, 120°01.76'W), near the mouth of the Truckee River, samples were collected at the surface and 25-, 150-, and 350-m depth (water column depth 385 m), and at the northern lake station (39°05.63'N, 120°09.00'W) samples were collected at the surface and 25-, 75-, and 150-m depths (water column depth 180

m). Surface samples were collected directly into 18-L stainless steel cans from the bow as the ship moved slowly forward to minimize ship-born contamination. Deep samples were collected using a 5-L flow-through sampler lowered from the side of the ship using a steel cable winch.

Water samples were filtered through a Whatman (Clifton, NJ, USA) GF/F, 90-mm-diameter filter (0.7- $\mu$ m nominal pore size) and the filtrate was extracted within 12 h of collection using a 10-g  $C_{18}$  solid-phase extraction cartridge (Isolute,  $C_{18}$  [EC], Jones Chromatography, Lakewood, CO, USA). Filters were baked at 400°C for 4 h and wrapped in clean aluminum foil before use. Cartridges were prepared using 60 ml methanol followed by 60 ml distilled water and were not allowed to go dry until the entire sample had been extracted. Water was pulled from the clean stainless steel cans through Teflon® tubing to the cartridge using a Supelco (Bellefonte, PA, USA) vacuum manifold attached to a vacuum pump. Three field blank cartridges were also prepared with methanol and distilled water and transported back to the laboratory for elution and analysis. Cartridges and filters were wrapped in aluminum foil and kept at -20°C until extracted.

Filters were extracted with chromatographic-grade dichloromethane solvent for 12 h using a Soxhlet extraction apparatus. Cartridges were eluted with 60 ml of 50:50 ethyl ether:petroleum ether (v/v). The elution solvent was allowed to drip through the cartridge slowly (1–2 ml/min). The filter and cartridge extracts from each sample were combined and

concentrated to 0.5 ml using rotary evaporation followed by a nitrogen gas blow down.

#### *Rain and snow*

Rain samples were collected at Ash Mountain site near the entrance to SNP (elevation 500 m) (Fig. 1) using an Aerochem (Bushell, FL, USA) automated wet and dry deposition sampler. Rainwater was collected in a clean, stainless steel bucket placed within the larger plastic container that opened only when the rain sensor is triggered by rainfall. Snow samples were collected at Ward Creek (elevation 2,200 m), approximately 2 km east of Ward Peak, west of Lake Tahoe and at Lower Kaweah (elevation 2,000 m) in the Sequoia National Forest. Snow samples were collected as soon as feasible (generally the next day) following a snow event. The top 2 to 3 cm of snow was collected using an aluminum snow shovel and placed into a 75-L aluminum can. The shovel and can were cleaned with detergent followed by rinsing with deionized water and chromatographic-grade acetone before use. The snow samples were allowed to melt slowly in closed containers at room temperature and the melted snow was then decanted into clean 18-L stainless steel canisters, which were kept sealed and cold (<5°C) until extracted. Samples were collected from December 1995 through April 1996. Sample volumes ranged from 0.45 to 4 L. Water was filtered as described above using a Whatman GF/F glass fiber (0.7- $\mu$ m nominal pore size). The filtrate was extracted using a 4-g C<sub>18</sub> cartridge (Isolute). Filters were not extracted in the case of rain and snow samples; therefore, concentrations presented in this report represent only the dissolved-phase concentrations.

#### *Analysis methods*

Samples were analyzed for trifluralin,  $\alpha$ - and  $\gamma$ -HCH, chlorpyrifos, chlorothalonil,  $\alpha$ - and  $\gamma$ -chlordane, *trans*-nonachlor, and  $\alpha$ - and  $\beta$ -endosulfan using a Hewlett Packard (Palo Alto, CA, USA) 5890 gas chromatograph coupled to a Hewlett Packard 5890A mass spectrometer in the negative chemical ionization (NCI), selected-ion monitoring mode. Methane was the ionization gas at a pressure of 200 Pa. The source temperature was 200°C and the quadrupole temperature was 100°C. Also, malathion and diazinon were analyzed using the same instrumentation in the electron impact (EI) mode. Source and quadrupole temperatures were also 200°C and 100°C, respectively. Gas chromatography conditions were as follows: 30-m DB-5 capillary column (J&W Scientific Corporation, Folsom, CA, USA), 0.25-mm inner diameter, 0.25- $\mu$ m film thickness, helium carrier gas, constant flow at 0.7 ml/min; temperature program: injector temperature 250°C, initial temperature 90°C, hold 1.0 min, 6°C/min to 280°C, hold 5 min, detector interface, 300°C. The ions monitored for each of the target compounds are listed in Table 1.

A mixture of diazinon-*d*<sub>10</sub> and PCB 204, 500 ng each, was added to standard mixtures and sample extracts just before analysis as internal standards. The diazinon-*d*<sub>10</sub> was used for quantification in EI mode and PCB 204 was used in NCI mode. Calibration standards ranged from 0.1 ng/ $\mu$ l to 0.005 ng/ $\mu$ l in NCI mode, whereas the range was 1.0 to 0.05 ng/ $\mu$ l in EI mode. A four-point calibration curve was established for each analyte and instrument response was linear over the range of calibration standards ( $r^2 \geq 0.99$ ). Typically, the instrument was recalibrated every 20 to 25 sample injections. Quantification of each analyte was calculated using the area of the ion with the largest abundance. Confirmation of a particular compound

in a sample extract was determined by the presence of at least one of the two qualifying ions in the proper ratio to the quantifying ion ( $\pm 20\%$ ). The requirement for only one qualifying ion in the proper ratio is due in large part to the use of the NCI mode where the number of ions in the mass spectra is often dominated by one or two ions, with very small contributions from other ions.

#### *Quality assurance-quality control*

The limits of detection (LODs) for each compound were calculated from analysis of extracts from distilled water blank cartridge experiments conducted in the field. For each blank, ion chromatograms of the quantifying ion for each compound were extracted from the total ion chromatogram and the largest peak within  $\pm 0.05$  min of the standard retention time was integrated and a concentration was calculated using the two lowest points of the calibration curve and the origin. The LOD for each compound was calculated from the average blank, in ng, plus three times the standard deviation of the blank. Six distilled water blanks were analyzed in the case of snow and rain samples, whereas three blanks were analyzed for the large-volume Lake Tahoe water samples. Sample concentrations were not blank corrected, with the exception of chlorpyrifos in Lake Tahoe water samples due to actual detection of small amounts of chlorpyrifos in blank extracts. The LOD values are listed in Table 1.

Collection efficiency of the solid-phase extraction cartridges was determined using ultrapure distilled water spiked with a mixture of the target pesticides at a concentration of 5 ng/L and processed in the same manner as the samples. Three collection efficiency experiments were conducted using 10 L of distilled water extracted with the 10-g C<sub>18</sub> cartridge, and three experiments were carried out using 4 L of distilled water with the 4-g C<sub>18</sub> cartridges. Recovery values from the six recovery experiments were similar. The solid-phase material in both types of cartridges was the same and the ratio of absorbent material to water volume was also the same. Recovery values ranged from 63 to 104%. Combined average recovery values for each compound are given in Table 1.

## RESULTS AND DISCUSSION

#### *Pesticide use data*

The Central Valley of California is one of the heaviest pesticide use areas in the USA. A number of orchard, vineyard, and row crops are treated with pesticides throughout the year including significant applications in the winter and early spring. The San Joaquin Valley, which comprises the southern part of the Central Valley, receives a larger volume of pesticide use than the Sacramento Valley, or northern section of the Central Valley. Detailed information on the usage of the pesticides included in our analyses was obtained from the State of California [18]. Within the four San Joaquin Valley counties (Fresno, Kings, Madera, and Tulare) closest to SNP, the total combined pesticide used during 1995 was 675,591 kg of chlorpyrifos, 264,064 kg of trifluralin, 232,629 kg of diazinon, 137,823 kg of chlorothalonil, 66,070 kg of endosulfan, and 28,683 kg of malathion applied to approximately 900,000 ha of harvested cropland. Cotton is by far the largest crop grown in these four counties at 333,000 ha followed by 142,000 ha of grapes, 85,000 ha of alfalfa, 59,000 ha of wheat, 50,000 ha of oranges, 40,000 ha of tomatoes, and other crops [19]. Considerable variation existed in pesticide use by month (Fig. 2).

Table 1. Ions monitored for gas chromatography–mass spectrometry analysis, limits of detection, spike recoveries, and environmentally significant physical properties of target pesticides<sup>a</sup>

Compound	Mass ions monitored	LOD Tahoe water (ng)	LOD Snow, rain (ng)	Average spike recovery (%) <sup>b</sup>	Vapor pressure (mPa)	Solubility (mg/L)	Henry's law constant (Pa m <sup>3</sup> /mol)	Log <i>K</i> <sub>ow</sub>	Log <i>K</i> <sub>oc</sub>
α-Chlordane	266, 237	0.12	0.12	96	1.3	0.056	9.51	6.00	4.78
γ-Chlordane	266, 264, 410	0.55	0.085	71	1.3	0.056	9.51	6.00	4.78
Chlorothalonil	266, 264, 268	0.14	2.3	93	0.076, 1.16 <sup>c</sup>	0.6	0.022	2.88	3.69
Chlorpyrifos	313, 315, 214	2.1	0.13	84	2.5	1.18	0.32 <sup>e</sup>	5.0	3.99
Diazinon	179, 137, 214	0.20	0.23	80	14.1	60	0.072	3.30	3.18
α-Endosulfan	242, 240	0.075	0.14	88	6.2 <sup>d</sup>	0.53 <sup>d</sup>	6.6 <sup>e</sup>	3.13	4.09
β-Endosulfan	406, 404, 408	0.076	0.19	74	3.2 <sup>d</sup>	0.28 <sup>d</sup>	0.87 <sup>e</sup>	3.62	3.37
α-HCH	255, 257, 71	0.034	0.072	75	3.33 <sup>e</sup>	7.8 <sup>f</sup>	0.68 <sup>f</sup>	3.46–3.89	3.28
γ-HCH	255, 257, 71	0.10	0.072	66	4.4	1.8 <sup>f</sup>	0.024 <sup>f</sup>	3.20–3.89	2.38–3.52
Malathion	127, 125, 158	0.40	0.19	82	0.45	145 <sup>d</sup>	0.00114	2.7	3.08
<i>trans</i> -nonachlor	300, 266, 237	0.11	0.36	83					
Trifluralin	335, 336, 305	0.020	0.39	80	14.6	0.32	10.3 <sup>g</sup>	5.07	3.85

<sup>a</sup> Values listed for physical properties of pesticides are selected values from the Herner [25] at temperatures 20–25°C unless otherwise indicated.

LOD = limit of detection; *K*<sub>ow</sub> = octanol–water partition coefficient; *K*<sub>oc</sub> = organic carbon partition coefficient; HCH = hexachlorocyclohexane.

<sup>b</sup> Spike recovery values are the average of 10-L and 4-L spike recovery experiments.

<sup>c</sup> Meylan and Howard [26] model estimation at 25°C.

<sup>d</sup> Determined at 25°C [38].

<sup>e</sup> [39].

<sup>f</sup> Determined at 23°C [40].

<sup>g</sup> Determined at 20°C [41].

Chlorpyrifos, diazinon, and endosulfan usage was greatest in August, whereas peak monthly usage of chlorothalonil was in February, of malathion was in March, and of trifluralin was in April. The majority of the applications to cotton and other major San Joaquin Valley row crops was by aircraft, whereas applications to orchards were primarily by speed sprayer ground rig. These methods can generate substantial airborne residue during applications and by postapplication volatilization [20,21]. Downwind pesticide deposition will occur through the processes of dry particle deposition, gas exchange onto foliage, soil, and surface waters, and through wet deposition in rainfall and snowfall.

### Precipitation

As described in earlier publications [12,22], air masses passing through California's Central Valley move eastward into the Sierra Nevada mountains; sample collectors were located within the path of this general air movement. The Sierra region receives the majority of its annual precipitation during the winter and early spring seasons. The 1995 through 1996 rain-equivalent precipitation season in the Sierra Nevadas (measured at Donner Summit in the central Sierras) was 210 cm [23]. The 1990 through 1996 annual mean was 130 cm, making the 1995 through 1996 season a relatively wet year. Total precipitation is most influenced by elevation. For example, the total precipitation (rain plus snow) for December 1, 1995, to April 30, 1996, for Ash Mountain (533 m) and Lower Kaweah (1,920 m) in SNP was 60 and 123 cm, respectively. For Ward Creek (2,200 m) in the Lake Tahoe basin, total precipitation was 127 cm for the same period.

Rain samples were collected at Ash Mountain (*n* = 7) and snow was collected at Lower Kaweah near the Giant Forest (*n* = 5) and at Ward Creek in the Lake Tahoe basin (*n* = 3) from December 1995 to April 1996. The amount of precipitation associated with each sample is shown in Table 2. Residues of all of the currently used pesticides (trifluralin, chlo-

rothalonil, chlorpyrifos, endosulfan, diazinon, and malathion) on our analytical target list as well as some of the organochlorine pesticides, α- and γ-HCH, were observed in at least some rain and snow samples (Table 2).

For the currently used pesticides, residues were of relatively high frequency and highest levels (to 85 ng/L) for chlorothalonil, a widely used fungicide. Ash Mountain in SNP showed the highest levels of this compound, in late February, March, and early April. These months, particularly February, correspond to the heaviest reported uses of chlorothalonil in the San Joaquin Valley counties west and northwest of SNP (Fig. 2). Chlorothalonil residues were generally lower at the Lower Kaweah site (1,920 m) than at the Ash Mountain (533 m) location, reflecting the effect of altitude, and perhaps more importantly distance, on residue load. The Lower Kaweah site is approximately 10 km northwest of Ash Mountain but 1,500 m higher in elevation and thus considerably more remote relative to the sprayed orchards and fields of the San Joaquin Valley. But still, Lower Kaweah showed higher chlorothalonil residues in late February, March, and April (2.3–13 ng/L) than during other winter–spring months, just as with the Ash Mountain site. Chlorothalonil residues did not exceed 1.7 ng/L in the three Ward Creek samples in the Lake Tahoe basin.

The presence of chlorothalonil in snow and rain samples is consistent with the physical properties listed in Table 1. The Henry's law constant, for example, is of the same approximate magnitude as for diazinon, γ-HCH, and others belonging to the low polarity, semivolatiles class of pesticides represented in Table 1. This compound has also been detected consistently in rain samples from the Chesapeake Bay region (MD, USA) [24]. According to the USDA Pesticide Database [25], the reported vapor pressure for chlorothalonil is low (0.076 mPa); however, model estimations of chlorothalonil vapor pressure using the modified Grain method [26] result in a value of 1.16 mPa. The published vapor pressure is also questionable in view of its relatively high Henry's law constant (0.022 Pa m<sup>3</sup>/mol).



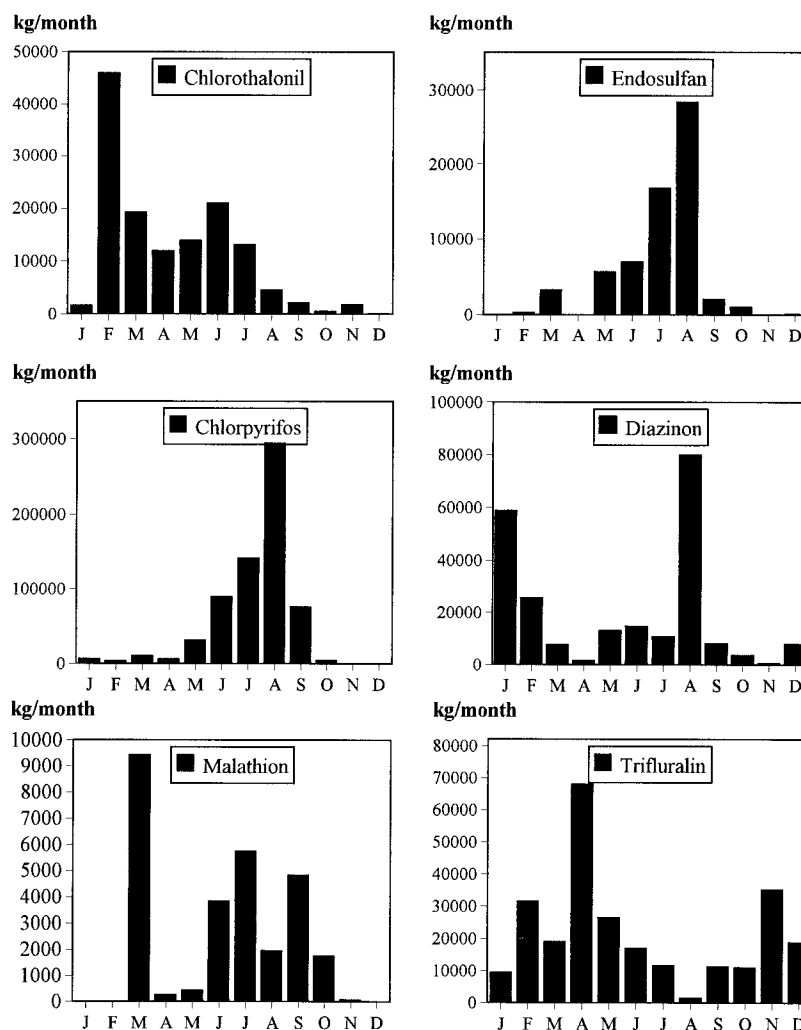


Fig. 2. Combined use of target pesticides during 1995 in Fresno, Kings, Madera, and Tulare counties, California, USA.

Table 2. Pesticide concentrations in rain and snow from the Sierra Nevada mountains (ng/L)<sup>a</sup>

Date collected	Precipitation (cm)	Volume (L)	Trifluralin	Chlorothalonil	Chlorpyrifos	Diazinon	Malathion	α-HCH	γ-HCH	α-Endosulfan	β-Endosulfan
Ash Mountain, Sequoia National Park											
December 14, 1995	6.5	4.0	<0.098	0.73	1.3	4.4	7.7	1.2	0.40	1.6	0.64
January 18, 1996	4.6	4.0	<0.098	0.97	2.3	19	3.6	1.4	0.52	<0.035	0.23
January 24, 1996	7.8	4.2	<0.098	<0.40	4.4	7.0	<0.046	1.4	0.53	0.86	0.27
February 1, 1996	0.99	0.75	<0.52	3.3	2.1	<0.31	<0.25	2.7	<0.096	<0.19	<0.25
February 26, 1996	15	4.3	1.2	85	4.4	6.8	24	4.2	1.7	6.5	1.4
March 30, 1996	0.66	0.45	<0.87	31	1.3	<0.51	<0.41	<0.16	<0.16	<0.31	<0.42
April 2, 1996	2.1	1.6	<0.35	13	3.1	<0.21	<0.17	1.7	<0.065	<0.13	<0.17
Lower Kaweah, Sequoia National Park											
January 18, 1996	11	2.5	<0.16	1.1	4.9	14	6.0	1.3	<0.029	0.97	<0.077
February 6, 1996	13	4.3	<0.098	<0.57	1.1	<0.057	<0.046	1.5	0.39	0.93	0.19
February 20, 1996	16	3.5	0.8	2.7	2.2	3.7	3.7	7.5	1.87	2.8	0.26
March 5, 1996	7.9	4.1	0.52	2.3	2.5	6.5	<0.045	1.7	0.49	1.0	<0.012
April 2, 1996	5.3	4.1	2.4	13	13	4.5	6.0	3.0	0.99	3.0	0.46
Ward Creek, Lake Tahoe basin											
December 20, 1995	2.5	4.0	<0.098	1.4	3.4	7.0	<0.046	0.59	<0.018	1.0	<0.012
February 2, 1996	9.8	4.0	<0.098	0.66	1.4	<0.057	18	0.45	<0.018	1.1	<0.012
April 7, 1996	1.6	4.0	<0.098	1.7	0.30	<0.057	6.9	<0.018	<0.018	<0.035	<0.012

<sup>a</sup> All Ash Mountain samples are rain and all Lower Kaweah and Ward Creek samples are snow. HCH = hexachlorocyclohexane.

We currently are in the process of verifying the vapor pressure and Henry's law constant of this compound. Nevertheless, it does appear that chlorothalonil is a persistent chemical, and evidence suggests that it can be atmospherically transported significant distances from application. These factors, combined with its heavy usage in the upwind agricultural valley, apparently lead to its deposition in the SNP winter precipitation.

For Ash Mountain, chlorpyrifos had a frequency of occurrence of 100% with peak concentrations in January and February (4.4 ng/L). Chlorpyrifos concentrations were less influenced by distance and elevation than was observed for chlorothalonil. At the Lower Kaweah site, results were similar to those from Ash Mountain from January to March (1.1–4.9 ng/L), and in April a concentration of 13 ng/L was observed at the Lower Kaweah site with only 3.1 ng/L at Ash Mountain. Usage of chlorpyrifos is substantial from January to May, but much more is applied from June through September with peak usage in August (Fig. 2). All three of the Ward Creek samples contained detectable chlorpyrifos. Concentrations ranged from 3.4 ng/L on December 20, 1995, to 0.30 ng/L on April 2, 1996 (Table 2).

Endosulfan was also detected in samples from all three locations with the highest concentration, 6.5 ng/L, of  $\alpha$ -endosulfan found in Ash Mountain rain on February 26, 1996. Similar concentrations of  $\alpha$ -endosulfan were observed at all three locations, generally 1 to 3 ng/L, with fewer detections of  $\beta$ -endosulfan at lower concentrations ranging from 0.19 to 1.4 ng/L. Use rates of endosulfan are low throughout the winter and early spring months with heaviest application during July and August. Higher concentrations of  $\alpha$ -endosulfan compared to those of  $\beta$ -endosulfan in precipitation are reflective of the technical mixture applied (expected  $\alpha$ : $\beta$  ratio = 7:3). Also, the  $\alpha$ -endosulfan isomer has a vapor pressure that is twice that of  $\beta$ -endosulfan (Table 1), and the  $\beta$  isomer has been shown to convert to the  $\alpha$  form while partitioning from water into the gas phase [27,28]. However,  $\beta$ -endosulfan is more soluble than the  $\alpha$  isomer and would likely be scavenged more easily by rainfall. Also, other researchers have found higher concentrations of  $\beta$ -endosulfan compared with  $\alpha$ -endosulfan in rain collected near the Great Lakes [29]. More study is needed to follow endosulfan concentrations in the air, surface water, snow, and rain to discern the processes controlling its fate in this alpine environment.

Diazinon had a frequency of occurrence of 57% in rain samples at Ash Mountain and 50% for all SNP samples. Highest levels were observed in the samples from January 18, 1996, with 19 ng/L at Ash Mountain and 14 ng/L at Lower Kaweah. Several samples from both SNP and Ward Creek had significant diazinon concentrations but without any obvious link to season, altitude, and location. Diazinon is a high-use, multi-purpose insecticide, with two peak usage periods in the San Joaquin Valley, in January as an orchard dormant spray and in August on a variety of crops.

Malathion was detected with frequency comparable to diazinon, 53%, in all SNP rain and snow samples, with peak concentrations in the Ash Mountain sample taken February 26, 1996 (24 ng/L) and the Tahoe Lake basin, Ward Creek sample taken February 2, 1996 (18 ng/L). For this chemical, as well as for trifluralin, the results lacked the seasonal, altitude, and location trends seen in the more robust data sets for chlorothalonil, chlorpyrifos, and diazinon. Neither  $\alpha$ -chlordane,  $\gamma$ -chlordane, nor *trans*-nonachlor was observed in any of the snow samples collected.

Table 3. Pesticides in Lake Tahoe water (ng/L)

Station/depth	Volume (L)	$\alpha$ -HCH <sup>a</sup>	$\gamma$ -HCH	Chloro-thalonil	Chlor-pyrifos	$\alpha$ -Endosulfan
South surface	9.0	0.27	0.45	1.4	3.5	<0.008
South 25 m	17	0.079	0.11	0.66	0.18	0.26
South 150 m	17	0.093	0.14	0.64	1.7	<0.004
South 350 m	17	0.026	0.10	0.47	1.3	<0.004
North surface	9.0	0.16	0.21	0.92	0.97	<0.008
North 25 m	10	0.38	0.33	1.3	4.2	0.031
North 75 m	10	0.15	0.20	0.99	1.2	0.14
North 150 m	10	0.26	0.39	3.2	2.9	<0.007

<sup>a</sup> HCH = hexachlorocyclohexane.

For the two organochlorine pesticides of historic use,  $\alpha$ - and  $\gamma$ -HCH,  $\alpha$ -HCH showed the highest frequency of occurrence in rain and snow above LOD, 70% of SNP samples, and the highest residue values (ranging up to 7.5 ng/L). Concentrations of both  $\alpha$ - and  $\gamma$ -HCH were similar at both SNP locations suggesting a more diffuse source than for the currently used compounds. The average 3:1 ratio of  $\alpha$ - to  $\gamma$ -HCH in our samples is on the lower end of the range of ratio values observed in air from different areas of the world [30–32], again supporting a global background source for these chemicals to our rain and snow samples. However,  $\gamma$ -HCH has a lower Henry's law constant than the  $\alpha$  isomer (Table 1), making it more easily scavenged from the gas phase of the atmosphere. Therefore, the  $\alpha$ -HCH: $\gamma$ -HCH ratio observed in the rain is probably lower than the ratio present in the atmosphere. Only the more abundant  $\alpha$  isomer was observed in Lake Tahoe basin snow samples.

#### Water

Large-volume (9–17-L) water samples were collected from four depths at two locations in Lake Tahoe in June 1995. The pattern of results is similar to those observed in snow samples from Ward Creek in that the two most abundant compounds were chlorothalonil (100% of samples; 0.47–3.2 ng/L) and chlorpyrifos (100% of samples; 0.18–4.2 ng/L) (Table 3). Lower concentrations (<1 ng/L) of  $\alpha$ - and  $\gamma$ -HCH and  $\alpha$ -endosulfan were also detected in the surface and deep water. Diazinon, malathion,  $\alpha$ - and  $\gamma$ -chlordane, and *trans*-nonachlor were not detected in these samples. No obvious trends occurred in concentration with depth, indicating that degradation rates are slower than input and subsequent mixing rates in the water column. Concentrations of all five compounds are in the same order of magnitude as observed in snow samples from the relatively pristine Ward Creek basin collected following three snowfalls during the 1995 through 1996 winter and early spring (Table 2). Precipitation, either falling on the lake surface (505 km<sup>2</sup>) or contributed from the proximate Lake Tahoe basin watershed (812 km<sup>2</sup>), is by far the largest contributor of water to the lake [33]; thus, wet deposition may be an important source of pesticides to the lake. However, other atmospheric processes such as dry particle and gas deposition are likely to be important as well. Moreover, the presence of these compounds in the Lake Tahoe water column is more evidence of a continuing long-term source of persistent organic pollutants to this region. However, more research is needed to link pesticides observed in precipitation with those observed in the lake. Some of the Lake Tahoe residues might have originated from local sources, given the significant private and commercial developments around the lake. The correspondence be-

Table 4. Summary of current-use pesticide measurements in California waters (ng/L)<sup>a</sup>

Source	Chlorpyrifos	Diazinon	Reference
Fogwater, Kearny Agricultural Center, 1989	900–14,200	7,200–76,300	[9]
Fogwater, Lindcove, 1991–1992	<1.3	<1.3–6,100	[12]
Rain, Lindcove, 1991–1992	<1.3–180	<1.3–2,000	[12]
Rain, Ash Mountain, 1991–1992	1.3–14	1.3–12	[12]
Rain, Lower Kaweah, 1991–1992	1.3–15	1.3–48	[12]
Rain, Ash Mountain, 1995–1996	1.3–3.9	<0.21–19	This study
Snow, Lower Kaweah, 1995–1996	1.1–13	<0.06–14	This study
Snow, Ward Creek, 1995–1996	0.30–3.4	<0.06–7.0	This study
Lake water, Tahoe, 1995	0.18–4.2	—	This study
San Joaquin River, 1992–1993	<10–220	<10–2,540	[34]

<sup>a</sup> Locations given in Figure 1.

tween the Ward Creek snow residue concentrations and those in the lake's surface water, although interesting, may be coincidental. A more detailed study of the influence of atmospheric transport processes in the Lake Tahoe basin is clearly needed.

To put results from precipitation and surface water in perspective with respect to level of contamination, Table 4 compares chlorpyrifos and diazinon concentration measurements in fogwater, precipitation, and surface waters from California. The highest reported concentrations are in Central Valley fogwater followed by rain collected in the Central Valley [9]. Rain from SNP, snow from the Lake Tahoe basin, and surface water from Lake Tahoe followed, in that order. Ranges of concentrations for the same two chemicals in San Joaquin River water samples from the Central Valley are higher than for the Sierra water samples, but only by factors of 10 to 50. The San Joaquin River, which is believed to receive residue input primarily from runoff from treated orchards and fields located near the river and its storm runoff channels, has experienced some localized fishkills believed to be due to pesticide residues [34].

With respect to aquatic toxicity, Sierra Nevada water concentrations are generally well below published median lethal concentration (LC50) values for representative aquatic organisms (Table 5), but in some cases, notably for chlorpyrifos, the LC50s for the amphipod *Gammarus fasciatus* (320 ng/L) are in the ng/L range, which is uncomfortably close to the observation here for southern Sierra Nevada rain samples. Another comparison is provided by U.S. Environmental Protection Agency and California state agency values for Acute Criteria to Protect Aquatic Life. These values, 83 ng/L for chlorpyrifos [35], 80 ng/L for diazinon [36], and 220 ng/L for endosulfan [37], are within a factor of 10 or less for some of our observed concentrations in rain and snow samples.

#### Estimates of atmospheric inputs to SNP

To place these results in some perspective, an annual atmospheric deposition loading of chlorpyrifos was estimated for SNP. As the majority of precipitation received in this region falls in the winter months, our data were used to estimate wet deposition loadings to the region. The average concentration of chlorpyrifos (4,800 ng/m<sup>3</sup>) from samples of snow from Lower Kaweah, a point that is approximately median for the park in terms of elevation and compass coordinates, was multiplied by the 1995 through 1996 precipitation total at this site (1.23 m) and by the area of the park (1.6 × 10<sup>9</sup> m<sup>2</sup>). The resulting value was 9.4 kg of chlorpyrifos deposited through wet deposition. An earlier estimate of wet deposition of chlorpyrifos to the region by Zabik and Seiber [12] resulted in a loading value of only 1.6 kg. This apparent discrepancy may be a result of a 50% increase in chlorpyrifos use in California from 1,035,574 kg in 1990 through 1991 to 1,493,206 in 1994 through 1995 [18].

A loading value for air–foliage dry deposition was recently estimated recently by Aston and Seiber [22] from analysis of pine needles sampled at the same Ash Mountain and Lower Kaweah sites (16 kg during the spring–summer season), and dry particle deposition was estimated by Zabik and Seiber [12] at 6 kg. The resulting annual atmospheric deposition flux rate of 150 to 190 mg/(ha y) or a total loading of 24 to 31 kg/y represents a low-end estimate because the dry particle deposition estimate was calculated from 1991 measurements when chlorpyrifos use was less. The estimate also does not include other deposition routes, such as vapor exchange with soil and surface water. In addition, data for the degradation product chlorpyrifos oxon was not included in the loading estimate. Conversion to the oxon is an important atmospheric process

Table 5. Ninety-six-hour median lethal concentration values (µg/L)<sup>a</sup>

Species	Chlorpyrifos	Chlorothalonil	Diazinon	Endosulfan	Malathion	Trifluralin
<i>Pteronarcys californica</i> (stonefly)	10		25	2.3	10	2,800
<i>Gammarus fasciatus</i> (amphipod)	0.32 <sup>b</sup>		0.2	6.0	0.76	2,200
<i>Pimephales promelas</i> (fathead minnow)	120 <sup>c</sup>		6,970 <sup>d</sup>	1.5	8,650	160
<i>Lepomis macrochirus</i> (bluegill)	2.4	26.3 <sup>e</sup>	168	1.2	87	135
<i>Oncorhynchus mykiss</i> (rainbow trout)	7.1	76 <sup>f</sup>	90	1.4	80	86

<sup>a</sup> all values are taken from Mayer and Ellersieck [42] unless otherwise noted.

<sup>b</sup> [43].

<sup>c</sup> [44].

<sup>d</sup> [45].

<sup>e</sup> [46].

<sup>f</sup> [47].

as evidence by significant concentrations observed in air samples collected at the Ash Mountain and Lower Kaweah sites during summertime sampling [22]. Much more work is needed to determine actual atmospheric loadings of chlorpyrifos and the other pesticides to the region.

Results of this study have serious implications for the Sierra Nevada mountains, as this area receives the majority of water inputs through rain and snow. Research in this area needs to be expanded to include measurements of all atmospheric inputs to this region throughout the year. Currently, studies are underway to determine whether the wintertime wet deposition residues translate into spring–summer surface water residues that might present exposures to aquatic life in the Sierra Nevada mountains.

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