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SUMMERTIME TRANSPORT OF CURRENT-USE PESTICIDES FROM CALIFORNIA'S CENTRAL VALLEY TO THE SIERRA NEVADA MOUNTAIN RANGE, USA

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(Received 20 October 1998; Accepted 30 March 1999)

Abstract—Agricultural activity in California's Central Valley may be an important source of pesticides that are transported in the air to the Sierra Nevada Mountain Range, USA. Pesticides applied to this intensive crop production area may volatilize under warm temperatures typical of the valley and be transported through the atmosphere to be deposited in the cooler, higher elevation regions of the Sierra Nevada Mountains. To determine the extent of summertime atmospheric transport of pesticides to this region, high-volume air, dry deposition, and surface water samples were collected in the Central Valley and at different elevations in California's Sequoia National Park. Results revealed that the highest residue concentrations were those of compounds with heavy summertime agricultural use. A significant drop in pesticide concentrations in both air and water samples was observed within a few 100-m elevation from the valley; however, levels remained relatively constant between ~500 and 2,000 m. Water concentrations from two areas above 3,000 m contained levels less than a tenth as high as those at lower elevations. Possible effects of the pesticides were estimated using measured water concentrations to calculate total exposure of three aquatic species to organophosphate insecticides. Aggregate exposure calculations showed concentrations were well below 96-h LC50 values for rainbow trout and stonefly but concentrations may be harmful to amphipods.

Keywords—Chlorpyrifos Endosulfan Sierra Nevada Mountains Atmospheric transport Deposition

INTRODUCTION

The ultimate fate of pesticides applied to agricultural fields is of great interest. Pesticides enter an air mass during application as spray drift, postapplication volatilization, and wind-blown erosion. Organochlorine pesticide residues continue to be found in remote regions, such as the Arctic, an apparent result of long-range atmospheric transport and deposition [1-4]. Currently used pesticides are generally less persistent in the environment and are not expected to undergo long-range transport, although as much as 90% of some currently used pesticides will volatilize within a few days of application depending on local conditions [5]. Few studies have been conducted concerning the regional airborne transport and potential effect of currently used pesticides on nontarget ecosystems. California's Central Valley, adjacent to the Sierra Nevada Mountains, presents a situation with unique potential for regional atmospheric transport of pesticides to a pristine ecosystem. Intense agriculture is practiced widely in a single, continuous valley (Central Valley) bounded to the west by coastal mountains and to the east by the Sierra Nevada Mountains. There is a total of 1.5×10^6 ha of cultivated land in the Central Valley, thus creating a source of immense area for the potential volatilization of pesticides [6]. The prevailing summertime wind patterns lead to a polluted air mass entering the Sierra Nevada Mountains from the central and coastal valleys. The summertime transport of pollutants, such as ozone, NO_x gases, particulate matter, and agricultural chemicals to the Sierra Nevada Mountain range has been well documented [7-9]

and has caused a degradation of the ecosystem [10]. Ozone originating in the Central Valley and coastal metropolitan areas has caused widespread, severe damage to foliage of the more sensitive Ponderosa (*Pinus ponderosa*) and Jeffrey pines (*Pinus jeffreyi*). Acid rain occurrences result in deposition of nitrate and sulfate in the Sierra Nevada [11]. Fine particulate matter regularly decreases visibility within the national parks in the Southern Sierra during the summer [7].

Concern over the deteriorating environmental quality of the Sierra Nevada has stimulated interest in the potential effects of other airborne toxicants on the Sierra Nevada Mountains. Exposure of wildlife, including declining amphibian populations, is of particular interest. Population declines of native frogs have been documented in Sequoia and Kings Canyon National Parks in the southern Sierra Nevada range [12-14]. Our earlier work has shown that organophosphate and other currently used pesticides, polychlorinated biphenyls, and *p,p'*-dichlorodiphenylethylene are present in surface waters, fish, and frogs at the 533-m elevation in Sequoia National Park [15], and that wintertime precipitation also contains pesticide residues [16]. This demonstrated that industrial chemicals and agrochemicals are present in wildlife, which is almost certainly the result of airborne deposition. These initial results have prompted us to continue to examine the links between agricultural activity in the Central Valley, atmospheric transport of toxins, and exposures in the Sierra Nevada.

The objective of this study was to determine the nature and extent of pesticide entry into the atmosphere and surface waters at different elevations in Sequoia National Park in the summer. Because little precipitation occurs in the summer, the primary deposition processes would be particle deposition and

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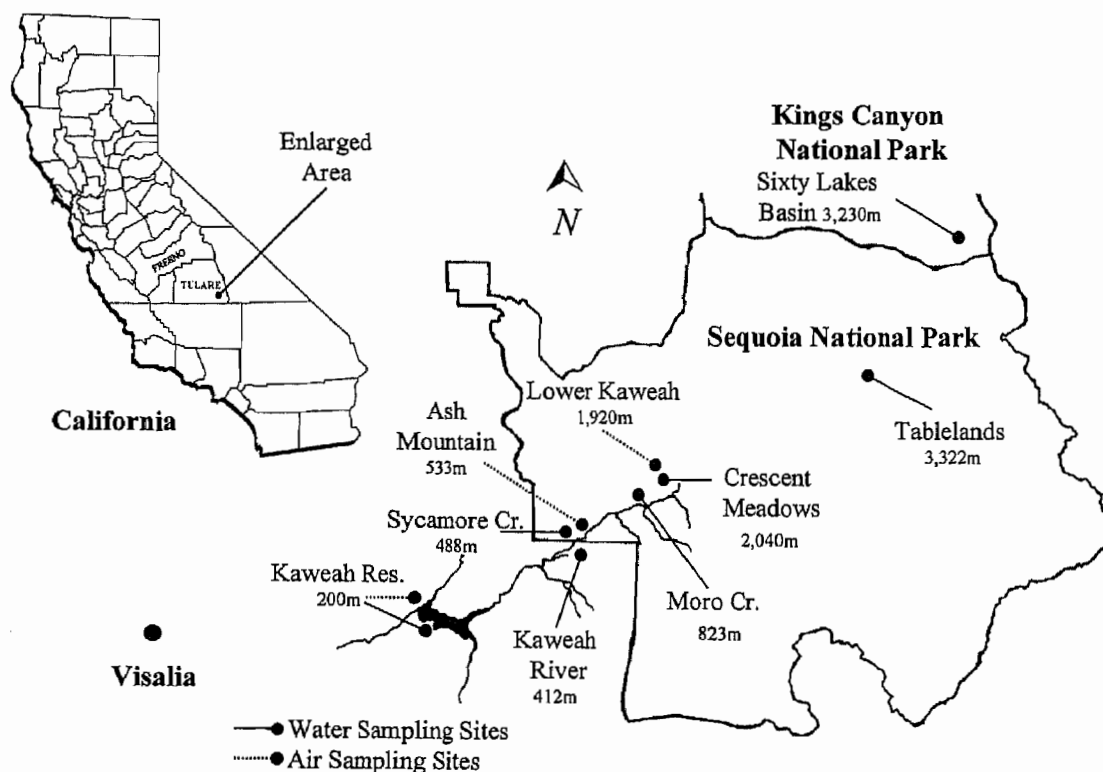


Fig. 1. Locations of sampling sites adjacent to and within Sequoia National Park, California, USA.

gas exchange with surface water, soil, and vegetation. Air and dry deposition samples were collected during the months of May to September 1996 at three elevations in the Sequoia National Park region (Fig. 1). On August 7, 1997, a 1-d surface water transect study was conducted from the Central Valley through Sequoia National Park to the 1,920-m elevation. During the week of August 21, 1997, additional surface water samples were collected from the 3,322-m elevation within the Sequoia National Park and the 3,230-m elevation of the Kings Canyon National Park. To assess the possible effects of the pesticides, a cumulative exposure calculation was conducted to determine the cumulative toxicity of organophosphorous compounds to very sensitive and typical species of the Sierra Nevada.

EXPERIMENTAL METHODS

Sampling and processing methods

Air samples were collected in duplicate for 8 h at the Kaweah Dam (200 m), Ash Mountain (533 m), and Lower Kaweah (1,920 m) using high-volume ($0.7 \text{ m}^3/\text{min}$) air samplers (Model TFIA, Staplex, Brooklyn, NY, USA), through 150 ml of pre-cleaned XAD-4 resin adsorbent. The average air sample volume collected was 250 m^3 . Air samplers collected the gas-phase fraction of the atmosphere. Duplicate air samplers were mounted on stands 1 m in height and spaced 2 m apart. Flow rates were measured at the beginning and the end of each sampling period using a rotometer flowmeter (Model VFC 123, Dwyer, Michigan City, IN, USA). The resin was contained within a 90-mm-diameter \times 17-mm-deep stainless steel cup with 0.1-mm no. 100 mesh screens at both ends. Extraction of the resin was performed as described by Zabik and Seiber [8]. Recovery of pesticides was determined by spiking glass with 100 ng of each pesticide and placing the glass wool in

series with the resin. The air samplers pulled air for no more than 8 h. Recoveries were acceptable given the volume of air sampled.

Surface water

Water samples were collected by dipping clean glass bottles below the surface of the water, rinsing them, and then allowing them to fill to their 4-L capacity. The samples were filtered through a Whatman (Clifton, NJ, USA) GF/F, 90-mm-diameter filter ($0.7\text{-}\mu\text{m}$ nominal pore size). Filters were baked at 200°C for 8 h and wrapped in clean aluminum foil before use. The filtrate was extracted using a 4-g C18 solid-phase extraction cartridge (Isolute, C18 [EC], Jones Chromatography, Lakewood, CO, USA). Cartridges were conditioned using 10 ml of methanol followed by 10 ml of distilled water and were not allowed to go dry until the entire sample had been extracted. The water was drawn from the bottles through Teflon[®] tubing to the cartridge, using a Supelco vacuum manifold (Bellefonte, PA, USA) attached to a vacuum pump. Cartridges were wrapped in aluminum foil and kept at -10°C until eluted. To remove the residues, the cartridge was eluted with three sequential elutions of 10 ml of ethyl acetate, 10 ml of 50/50 ethyl acetate-dichloromethane, and 10 ml of dichloromethane. Filters contained too little particulate matter to warrant analysis. Recoveries were determined by spiking six replicates of 4-L volumes of distilled water at 10 ng/L and processing each replicate as outlined above. Recovery values ranged from 54 to 115% and were averaged and listed in Table 1.

Dry particulate

Dry particulate deposition samples were collected at Kaweah Reservoir (200-m elevation), Ash Mountain (533-m elevation), and Lower Kaweah (1,920-m elevation) using an au-

Table 1. Ions monitored for gas chromatography-mass spectrometry analysis, limits of detection and spike recoveries

Compound	Mass of ions monitored (m/z)	Limits of detection		Average spike recovery	
		Water (ng)	Air (pg/m ³)	Water (%)	Air (%)
Chlorpyrifos	313,315,214	2.1	0.5	84	72
Chlorpyrifos oxon	297,298,299	1.5	0.8	75	88
Diazinon	179,137,214	0.2	1.0	80	77
Chlorothalonil	264,266,268	2.3	1.5	90	82
Endosulfan I	240,242	0.07	0.6	88	83
Endosulfan II	406,404,408	0.07	1.0	74	80
Endosulfate	384,386,388	0.09	0.9	65	75
Malathion	127,125,158	0.40	1.0	82	72
Trifluralin	335,336,305	0.02	1.6	80	81

tomated wet/dry particulate deposition sampler (Aerochem, Bushnell, FL, USA). A clean glass plate 25 cm in diameter was placed in a polyethylene bucket on the dry particulate side of the sampler and allowed to collect particulate matter over a 4-week period. The plate was thoroughly cleaned between each sampling with ethyl acetate. Blanks were collected into precleaned 100-ml amber glass jars before a sampling period by rinsing the cleaned plate with ethyl acetate. Samples were likewise collected after the 4-week period. A paper Kimwipe (Kimberly-Clark, Roswell, GA, USA) was used to aid in the removal of dry particulate deposition and placed in the jar along with the solvent. After shaking the jar with the solvent and the Kimwipe for 30 min, the solvent was removed and concentrated before analysis.

Analysis

Samples were analyzed for trifluralin, chlorpyrifos, chlorpyrifos oxon, chlorothalonil, endosulfan I and II, malathion, and diazinon using a Hewlett Packard 5890 gas chromatograph coupled to a Hewlett Packard 5989A mass spectrometer (Hewlett Packard, Avondale, PA, USA) in the negative chemical ionization mode. Methane was the ionization gas at a pressure of 200 Pa. Malathion and diazinon were analyzed in the electron impact mode. The source temperature was 150°C, and the quadrupole temperature was 100°C. Gas chromatography conditions were as follows: 25-m DB-5 capillary column (J&W Scientific, Folsom, CA, USA), 0.20-mm i.d., 0.25- μ m film thickness, and helium carrier gas at a constant flow of 0.7 ml/min. The temperature program was as follows: 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 (Table 1).

Diazinon-d₁₀, 500 ng, was added to standard mixtures and sample extracts as an internal standard. Calibration standards ranged from 0.1 to 0.005 ng/ μ l in the negative chemical ionization mode. A four-point calibration curve was established for each analyte, and instrument response was linear over the range of calibration standards ($r^2 > 0.99$). Typically, the instrument was recalibrated after every 20 to 25 sample injections. Quantification of each analyte was calculated using the area of the ion with the maximum abundance. Confirmation of a particular compound in a sample extract was determined by the presence of at least one of the two qualifying ions.

Quality assurance/quality control

The instrumental limits of detection for each compound were calculated from the analysis of extracts from distilled

water blank cartridges and XAD-4 resin. No interfering peaks were found in the blank samples. For each blank, ion chromatograms of the quantifying ion for each compound were extracted from the single-ion chromatogram, and the largest peak within ± 0.05 min of the standard retention time was integrated and the concentration calculated using the two lowest points of the calibration curve and the origin. The limits of detection for each compound was calculated from the average blank, in nanograms, as three times the standard deviation of the blank.

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.

RESULTS AND DISCUSSION

Pesticide use data

Detailed information on pesticide usage was collected for Fresno and Tulare counties (Table 2) [17]. Tulare and Fresno are immediately upwind of the park's entrance and represent the greatest potential source for pesticide emission. The predominant wind direction during the summer months is from the northwest to the southeast [18]. The pesticides applied in largest amounts during the summer months, in decreasing order of usage, are chlorpyrifos, chlorothalonil, endosulfan, diazinon, and malathion. Malathion usage in agriculture was not significant at any time, although this chemical has widespread home, garden, and mosquito-abatement applications. Because malathion does not require a permit, the reported values do not necessarily reflect actual use patterns.

In reviewing the application records for the two counties, the most striking difference is the usage pattern for chlorothalonil, a foliar fungicide. Chlorothalonil has wider use in Fresno for melon and cucurbit crops. Chlorpyrifos, diazinon, and malathion are organophosphate insecticides. Chlorpyrifos is a common dormant spray applied to peach, almond, and nectarine orchards in winter; however, its greatest use is during summer as a foliar insecticide on cotton, citrus, and other crops. Diazinon is used as a dormant spray on orchards in the winter and as a general insecticide applied to many crops throughout the year. Endosulfan is one of the few organochlorine insecticides still in use; it is primarily used on cotton but is applied to other summer crops such as melons and tomatoes. Trifluralin is a broad leaf preemergence herbicide cultivated in fields before planting. These application data are indicative of the frequency and magnitude of pesticide use and

Table 2. Fresno and Tulare pesticide application data for 1995 (Kg a.i./month)

	Chlorothalonil	Chlorpyrifos	Diazinon	Endosulfan	Malathion	Trifluralin
Fresno						
January	1,365	4,696	30,218	2	0	29
February	24,197	2,776	12,411	383	14	7,832
March	11,319	4,360	3,967	3,385	1,500	6,023
April	10,470	980	860	38	140	37,129
May	10,835	2,920	7,554	1,008	230	20,161
June	18,538	16,393	9,016	4,614	1,104	12,093
July	10,112	47,476	5,888	11,190	2,280	8,884
August	4,237	141,899	7,021	13,220	735	1,475
September	2,159	45,885	4,138	1,552	42	3,139
October	442	933	3,479	1,142	417	7,228
November	130	216	140	167	71	25,330
December	206	357	3,911	164	36	6,706
Tulare						
January	249	1,592	18,224	58	2	5,388
February	16,536	1,010	9,979	47	0	15,162
March	4,099	3,977	1,048	9	2,993	5,902
April	121	5,115	368	41	153	12,266
May	28	19,597	3,084	4,558	245	2,294
June	162	62,573	419	1,871	177	612
July	0	43,669	998	3,217	830	560
August	245	55,341	433	3,571	893	202
September	0	8,679	78	87	4,456	52
October	0	4,592	75	0	1,366	915
November	327	379	0	0	34	1,016
December	0	220	3,850	49	1	329

represent the potential emission source for atmospheric volatilization and transport.

Air samples

The potential of pollutant transport into the Sequoia National Park is dependent on the season. Inversion conditions largely limit wintertime atmospheric transport of pesticides to the Sequoia National Park from the Central Valley. Pollutants are likely to enter the park when storm systems break up the inversion and deposit pesticides through wet deposition [16]. In contrast, summer wind patterns bring polluted air originating in the Central Valley into the Sierra Nevada Mountains. During the day, an upslope breeze carries pollutants originating from the Central Valley into the Sequoia National Park. During the night, the predominant flow is downslope [19].

Duplicate air samples were collected at Kaweah Reservoir (200 m) once a month for 8 h from May to September 1996. Air was sampled on the same dates at Ash Mountain (533 m)

except in August when a forest fire denied access to the road. The Lower Kaweah site was sampled on the same dates, but only from July to September. Residues of all currently used pesticides analyzed (trifluralin, chlorothalonil, chlorpyrifos, endosulfan, diazinon, and malathion) were observed at least once during the summer (Table 3). The difference between duplicate air samples did not vary more than 40% for any of the pesticides monitored.

The predominant pesticides detected in the air mass during the summer of 1996 were chlorpyrifos and its oxon, followed by endosulfan I and II, chlorothalonil, and low concentrations of diazinon. The highest concentrations of airborne pesticides were detected at the Kaweah Reservoir (200 m) (Table 3). This site is adjacent to citrus orchards that receive summer applications of chlorpyrifos and potentially other pesticides. Concentrations of chlorpyrifos were highest in June (17.5 ng/m³), and those of chlorpyrifos oxon were highest in May (30.4 ng/m³). As May and June are the months of maximum use of

Table 3. Pesticide concentrations in air at three elevations (ng/m³)

Location	Date	Trifluralin	Diazinon	Chlorpyrifos	Chlorpyrifos oxon	Malathion	Chlorothalonil	Endosulfan I	Endosulfan II	Endosulfate
Kaweah Reservoir—200 m	5/30/96	0.27	0.23	ND ^a	30.37	0.29	ND	3.67	0.18	0.01
	6/25/96	0.18	0.24	17.5	4.89	0.4	ND	1.15	0.34	0.01
	7/10/96	0.13	ND	2.1	11.74	ND	ND	2.3	0.4	0.05
	8/16/96	0.13	ND	1.08	6.04	ND	1.1	1.13	0.27	0.05
	9/21/96	0.64	ND	2.14	18.84	ND	1.93	1.34	0.64	0.07
Ash Mountain—533 m	5/30/96	0.17	0.12	1.71	2.86	0.15	ND	1.07	0.07	0.01
	6/25/96	0.03	0.07	0.9	0.94	ND	ND	0.53	0.13	0.01
	7/10/96	0.07	ND	0.05	0.52	ND	ND	1.5	0.19	0.04
	9/21/96	0.27	ND	0.22	1.74	ND	1.31	0.52	0.12	0.02
Lower Kaweah—1,920 m	7/10/96	0.13	ND	0.35	1.17	ND	0.24	1.52	0.23	0.03
	8/16/96	0.28	ND	0.16	0.19	ND	0.92	0.55	0.09	0.02
	9/21/96	0.25	0.18	0.2	0.1	ND	1.6	0.3	0.14	0.02

^a ND = not determined.

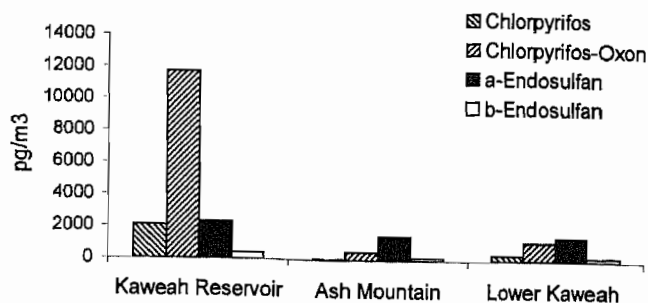


Fig. 2. Pesticide concentrations in air at three elevations.

chlorpyrifos, these results are consistent with the expected source strength.

The formulation of endosulfan contains a 70:30 mixture of endosulfan I and II, respectively. Endosulfan I has a higher vapor pressure than endosulfan II [20,21], and the field-plot studies have shown that endosulfan I volatilizes from soil at a much higher rate than does endosulfan II [22]. Residues of both endosulfan I and II were present in air at all sites throughout the summer, and the highest concentrations of both endosulfan isomers were found at the 200-m elevation. As expected, endosulfan I was always in higher concentration than endosulfan II. The highest observed concentration of endosulfan I was 3.7 ng/m³ in May and that of endosulfan II was 0.64 ng/m³ in September.

At the Ash Mountain site (533 m), all air concentrations of pesticides dropped significantly relative to the Kaweah Reservoir, which is about 18 km to the west. Chlorpyrifos, chlorpyrifos oxon, and endosulfan I and II residues were the most frequently measured above the limit of detection. Of the two, the Lower Kaweah site (1,920-m elevation) had the lowest air concentrations of pesticides. Aston and Seiber [9] showed a dilution in organophosphate pesticide concentrations in air with increasing elevation from Lindcove Station (112 m) to Lower Kaweah (1,920 m). Foliar absorption and oxidation losses were indicated as the primary dissipation pathways. The current results show a significant decline in pesticide concentrations from the Kaweah Reservoir (200 m) to Ash Mountain (500 m) (Mann-Whitney test, $p < 0.05$) for all pesticide types studied, but no significant decrease in pesticide concentrations from Ash Mountain to Lower Kaweah (Mann-Whitney test, $p > 0.1$). This is clearly demonstrated for chlorpyrifos and endosulfan, which are the pesticides detected with maximum frequency in air during the summer (Fig. 2). The decline in concentrations from Kaweah Reservoir to Ash Mountain was ≈60%. The difference between the previous report [9] and the current results can be explained by the differences in the sam-

pling protocol. Aston and Seiber sampled air for a 24-h period, an interval that encompassed both daytime upslope and evening downslope air transport. The downslope current would be less polluted and results in lower overall concentrations, particularly for the 1,920- and 533-m elevations. Upslope breezes of 1 to 2 m/s in the morning reverse to downslope breezes in the evening, which can continue for most of the night, forming a consistent pattern [23]. The current results agree with the findings for ozone and particulate matter [7], which illustrate a very efficient upslope air transport from Ash Mountain (500 m) to Lower Kaweah (1,920 m), and thus, little difference in concentrations for samples collected during the daytime.

Chlorothalonil was present at all three sampling sites at the end of the summer of 1996. The application records indicate that its peak application time was in June 1996, but it does not appear in significant concentrations until the end of summer, when applications had declined. The concentrations were not significantly different at the three elevations, thus illustrating the atmospheric stability of chlorothalonil and its potential for long-range transport. Model estimates indicate that atmospheric oxidative half-life of chlorothalonil is greater than 1,700 d [24]. The vapor pressure of chlorothalonil is reported to be low, 13 mPa [25], yet it was present in relatively high concentrations at the 500-m elevation during winter precipitation [16], indicating significant wintertime volatilization. In the present study, it was seen at relatively high concentrations in late summer air sampling at all elevations. The finding that chlorothalonil peak concentrations were reached at late summer, whereas peak application was in June, may be due to chlorothalonil having a slow, steady, and somewhat prolonged volatilization rate from the sites of application [26]. There could also be significant transport on windblown, airborne particulate matter originating from the treated fields.

Dry deposition

Dry deposition is an important means of contaminant transport, but it can be difficult to measure because of spatial and temporal variations and the lack of standardized techniques [27,28]. In this study, clear glass plates served as the surrogate surface.

The pesticides found in the dry deposition samplers correlated well with the pesticide residues in the highest concentrations in air and those of the maximum reported applications during the summer months (Table 4). Chlorpyrifos and chlorpyrifos oxon are present at each of the sites with the oxon consistently higher than the parent thion; this supports the air concentration data. This agrees with the results of Aston and Seiber [29] for chlorpyrifos residues in pine needles. Endosulfan I and II were present at low concentrations. These dry

Table 4. Pesticide concentrations in dry deposition at three elevations (ng/m²/day)

Location	Date	Chlorothalonil	Chlorpyrifos	Chlorpyrifos		
				oxon	Endosulfan I	Endosulfan II
Kaweah Reservoir—200 m	7/10/96	10	24	80	0.4	1.8
	9/20/96	18	1.5	1.5	ND ^a	3.6
Ash Mountain—533 m	6/27/96	ND	0.3	ND	ND	ND
	7/10/96	3.5	3	23	ND	ND
Lower Kaweah—1,920 m	6/27/96	1	0.8	15	ND	ND
	8/16/96	6	3	15	0.7	ND
	9/20/96	2	0.2	ND	ND	ND

^a ND = not determined.

Table 5. Pesticide concentrations in a surface water transect from the Central Valley to the Sierra Nevada (ng/L)

Elevation (m)	Trifluralin	Diazinon	Chlorothalonil	Chlorpyrifos	Chlorpyrifos oxon	Malathion	Endosulfan I	Endosulfan II
118	108.12	74.1	6.62	122.4	39.2	83	24.8	140.5
213	85.45	69.51	5.09	99.32	30.91	64.97	17.42	89.39
411	77.46	63.5	6.05	89.31	24.66	65.61	17.79	87.35
488	73.44	72.79	5.16	96.71	24.94	72.5	16.68	99.65
823	90.67	66.06	1.94	104.25	33.3	66.12	16.96	90.83
2,042	96.02	65.11	6.59	118.15	37.22	81.61	18.42	101.86
3,231	1.2	0.92	<LOD ^a	0.195	<LOD	<LOD	0.34	1.0
3,322	<LOD	3.23	<LOD	6.17	<LOD	<LOD	0.9	0.41

^a LOD = limit of detection.

deposition results, a qualitative assessment of summertime loading, show a trend of decreasing concentration with an increase in elevation.

Surface water

During the subsequent summer of 1997, surface water samples were collected. Table 5 represents the average of duplicate water samples. The duplicates did not vary by more than 11% except for the samples taken at Moro Creek, California, USA, where the samples varied by 50%. The pesticides consistently in the highest concentrations in the surface waters were chlorpyrifos and endosulfan, which is expected, given that these two pesticides have peak usage during the summer months [17].

The chlorpyrifos/chlorpyrifos oxon ratio in surface waters is opposite to that found in air; chlorpyrifos was found in higher concentrations than the oxon in water. Both forms are transported during winter and summer and have the potential to be deposited as both wet and dry deposition. The formation of the oxon in the atmosphere is more efficient during the summer because of increased sunlight and oxidants in the air. The oxon appears to be stable in air and on dry surfaces [9]. The higher concentrations of the parent chlorpyrifos may be due to deposition during winter and release to surface water from summer melt [16]. The oxon may be less stable in water than the parent because of the polarizing effect of the oxygen atom, thereby making it more susceptible to hydrolysis.

Endosulfan I and chlorothalonil had the lowest pesticide concentrations throughout the transect. The endosulfan I concentrations were significantly lower than the endosulfan II; this is to be expected because the water solubility of endosulfan I is calculated to be 3.7 mg/L, whereas it is 21 mg/L for endosulfan II [20]. Endosulfan II has been found to be the predominant form in rain samples [30]. Chlorothalonil was consistently found at low concentrations in sampled surface waters, which is to be expected because it also has a relatively low water solubility of 106 mg/L [24].

All pesticide concentrations dropped significantly in surface water above the 2,040-m elevation. This suggests that pollutants entering the Kaweah Canyon are not effectively transported to higher elevations. Earlier work on the transport of aerosols within the Kaweah Canyon by Ewell et al. [19] supports this conclusion. Ewell et al. determined that pollutant profiles differed between lower and higher elevations because of differences in air masses. The 200- and the 533-m sites are more affected by the pollution generated in the San Joaquin Valley because these sites are within the wind circulation of the Central Valley. Pollutant profiles at 2,000 m and above are decoupled from the lower elevations and tend to have pollutant

profiles indicative of long-range transport. The decrease in pollutant concentrations with increasing elevation contrasts with what Blais et al. [31] predicted for temperate-zone mountain regions near pollutant sources. Blais et al. suggested that a cold-condensation effect would enhance pollutant concentrations of semivolatile organochlorine with an increase in altitude. In the case of the southern Sierra Nevada Mountain range, a cold condensation effect does not occur partly due to meteorological conditions that do not favor transport to higher elevations.

Potential effects

The potential for cumulative effects of organophosphorous pesticides on aquatic biota in Sequoia National Park was estimated using the concentrations observed in the surface water as the exposure concentrations. Similar calculations have been made for the congeners of polychlorinated biphenyls [32] and for other chemicals that act by the same toxic mechanism [33]. The reference species chosen were the amphipod (*Gammarus fasciatus*), stonefly (*Pteronarcys californica*), and rainbow trout (*Oncorhynchus mykiss*) because toxicity data were available for all of the organophosphorous compounds in relation to these species, and because these species are found in the Sierra Nevada Mountains (Table 6). The amphipod and stonefly represent some of the most sensitive species, whereas the rainbow trout is more typical of vertebrates.

The organophosphate with the highest toxicity for each species was chosen as the reference compound for normalizing the other two. Chlorpyrifos was chosen for the stonefly and the rainbow trout, whereas diazinon was chosen for the amphipod. Dividing each into the reference compound value for that particular species normalized the LC50 values for each species. The normalized values represent the toxic equivalent factor [34]. These normalized values were then multiplied by their corresponding concentrations observed at the 2,040-m elevation. The results for each chemical were then multiplied by 2 to account for additional contribution to toxicity from the oxygen analogues. Oxon toxicity was assumed to be equal to the corresponding thions in this calculation. The calculation is a conservative estimate because it is known that the oxygen analogues can potentially be many times more toxic than the parent [35]; however, there are little aquatic toxicity data available for the oxons. The three values for each species were added to yield total exposure in units of micrograms per liter. The 96-h LC50 concentration for chlorpyrifos is 10 µg/L for the stonefly, whereas the calculated total exposure was 0.45 µg/L for the three organophosphorous compounds. The total exposure of the mixture is approximately a factor of 22 lower than the 96-h LC50. Similar conclusions can be drawn for the

Table 6. Ninety-six hour, LC50 values ($\mu\text{g/L}$)^a and calculated total exposure equivalence ($\mu\text{g/L}$)

Species	Chlorpyrifos	Diazinon	Malathion	Total exposure equivalence ($\mu\text{g/L}$)
<i>Pteronarcys californica</i> (Stonefly)	10	25	10	0.45
<i>Gammarus fasciatus</i> (Amphipod)	0.32 ^b	0.2	0.76	0.32
<i>Oncorhynchus mykiss</i> (Rainbow trout)	7.1	90	80	0.25

^a All values are taken from Mayer and Ellersieck [37], unless otherwise noted.

^b [38].

rainbow trout; the cumulative exposure is 0.25 $\mu\text{g/L}$, a factor of 28 lower than the acute toxic value of 7.1 $\mu\text{g/L}$. Similarly for diazinon, there may be times when aggregate effects reach harmful concentrations to the more sensitive species, in this case, the amphipod. The 96-h LC50 for the amphipod is 0.2 $\mu\text{g/L}$, and the calculated total exposure was above this, at 0.32 $\mu\text{g/L}$. Our measured concentrations in surface water may not be representative of values throughout the year because they were collected at the end of the summer when surface water volume is at its lowest, and pesticide dry deposition is at or near its highest. Furthermore, total exposure calculations as provided here require assumptions that may not accurately reflect the true environment.

CONCLUSIONS

The residues in highest concentration correlate to application reports in the Central Valley. Previous reports have suggested that pesticide concentrations decrease with an increase in elevation, but we found this to be the case only at the lower elevations. Air samples taken during the summer of 1996 showed a dilution of 1.7 from the 200- to the 533-m elevation; however, no significant dilution was shown from the 533- to the 1,920-m elevation. Surface waters contained low concentrations (nanograms per liter) of pesticides, apparently from both winter and summer depositions. The pesticides in highest concentrations in the surface water were primarily the pesticides used in summer, chlorpyrifos and endosulfan. Peak concentrations in air and water correlated roughly with peak application periods in the Central Valley in summer. Concentrations of pesticides in surface water declined significantly past the 2,040-m elevation.

The concentrations of individual pesticides in surface waters were below acute toxicity values, but when considering the cumulative exposures of organophosphate pesticides, there is still concern of exposures to the more sensitive species in the Sierra Nevada ecosystem. Several of the compounds measured (chlorpyrifos, endosulfan, trifluralin, and malathion) are potential or suspected environmental endocrine disruptors [36]. This aspect, although not studied here, may warrant future attention. The additive and synergistic effects of these pesticides must be considered to determine the total effect of agricultural residues on the ecosystem.

Acknowledgement—The assistance of Annie Esperanza and Harold Werner and other personnel of Sequoia National Park research section is gratefully acknowledged. This work was supported by the U.S. Department of Agriculture–Natural Resources Institute Grant 95-37102-2433 to the University of Nevada.

REFERENCES

- Cotham WE, Bidleman TF. 1991. Estimating the atmospheric deposition of organochlorine contaminants to the Arctic. *Chemosphere* 22:165–188.
- Fellin P, Barrie LA, Dougherty D, Toom D, Muir D, Grift N, Lockhart L, Billeck B. 1996. Air monitoring in the Arctic: Results for selected persistent organic pollutants for 1992. *Environ Toxicol Chem* 15:253–261.
- Gregor DJ, Gummar WD. 1989. Evidence of atmospheric transport and deposition of organochlorine pesticides and polychlorinated biphenyls in Canadian Arctic snow. *Environ Sci Technol* 23:561–565.
- Rice CP, Chernyak SM. 1997. Marine Arctic fog: An accumulator of currently used pesticide. *Chemosphere* 35:867–878.
- Taylor AW. 1978. Postapplication volatilization of pesticides under field conditions. *J Air Pollut Control Assoc* 17:277–283.
- California Agricultural Statistics Service. 1992. *California Statistical Abstract*. Sacramento, CA, USA.
- Cahill TA. 1989. Monitoring of atmospheric particles and ozone in Sequoia National Park: 1985–1987. Final Report on Contract A5-180-32. California Air Resources Board, Sacramento, CA, USA.
- Zabik J, Seiber JN. 1993. Atmospheric transport of organophosphate pesticides from California's Central Valley to the Sierra Nevada Mountains. *J Environ Qual* 22:80–90.
- Aston L, Seiber JN. 1997. The fate of summertime airborne organophosphate pesticide residues in the Sierra Nevada mountains. *J Environ Qual* 26:1483–1492.
- Duriscoe DM. 1987. Evaluation of ozone injury to selected tree species in Sequoia and Kings Canyon National Parks, 1985 survey results. Air Quality Division, National Park Service, Denver, CO, USA.
- Unger CD. 1989. Analysis of a summertime acid rain event in the Sierra Nevada. *Proceedings, Air and Waste Management Association Symposium on Effects of Air Pollution on Western Forests*, Anaheim, CA, USA, June 3–5, pp 137–146.
- Bradford DF, Graber DM, Tabatabai F. 1994. Population declines of the native frog, *Rana muscosa*, in Sequoia and Kings Canyon National Parks, California. *Southwest Nat* 39:323–327.
- Drost CA, Fellers GM. 1996. Collapse of a regional frog fauna in the Yosemite area of the California Sierra Nevada, USA. *Conserv Biol* 10:414–425.
- Jennings MR. 1996. Status of Amphibians. Sierra Nevada Ecosystem Project: Final Report to Congress, Vol II—Assessments and Scientific Basis for Management Options. Report 37. University of California Davis, Davis, CA, USA.
- 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.
- McConnell LL, LeNoir J, Datta S, Seiber JN. 1998. Wet deposition of current-use pesticides in the Sierra Nevada Mountain range. *Environ Toxicol Chem* 17:1908–1916.
- University of California, Davis. 1994. *Integrated Pest Management Database*. Davis, CA, USA.
- Hayes TP, Kinney JJR, Wheeler NJM. 1984. *California Surface Wind Climatology*. State of California Air Resources Board Aerometric Data Division. Sacramento, CA, USA.
- Ewell DM, Flocchini RG, Myrup LO, Cahill TA. 1989. Aerosol

- transport in the southern Sierra-Nevada. *J Appl Meteor* 18:112-125.
20. Schmidt WF, Hapeman CJ, Fettinger JC, Rice CP, Bilboulia S. 1997. Structure and asymmetry in the isomeric conversion of β to α endosulfan. *J Agric Food Chem* 45:1023-1026.
 21. Rice CP, Chernyak SM, Hapeman CJ, Bilboulia S. 1997. Air-water distribution of the endosulfan isomers. *J Environ Qual* 26:1101-1106.
 22. Rice CP, Nochetto CB, Zara P. 1999. Volatilization of trifluralin, atrazine, metolachlor, chlorpyrifos, endosulfan I, and endosulfan II from freshly tilled soil. In Rice CP, Sillman S, eds, *Pesticide Emission Model Development*, Final Project Report. U.S. Environmental Protection Agency, Research Triangle Park, NC.
 23. U.S. National Park Service. 1996. Meteorological annual data summary. Report NPSD-369. Lakewood, CO.
 24. Meylan W. 1996. *Atmospheric Oxidation Program*, Ver 1.8. Syracuse Research Corporation, Syracuse, NY, USA.
 25. Kidd H, James DR. 1991. *Agrochemicals Handbook*, 3rd ed. Royal Society of Chemistry Information Services, Cambridge, UK.
 26. Van den Berg F, Bor G, Smidt RA, van de Peppel-Groen AE, Smelt JH, Muller T, Maurer T. 1995. Volatilization of parathion and chlorothalonil after spraying onto a potato crop. Report 102. DLO Winand Staring Centre, Wageningen, The Netherlands.
 27. Holsen TM, Noll KE. 1992. Dry deposition of atmospheric particles: Application of current models to ambient data. *Environ Sci Technol* 26:1807-1815.
 28. Pirrone N, Keeler GJ, Holsen TA. 1995. Dry deposition of semivolatile organic compounds to Lake Michigan. *Environ Sci Technol* 29:2123-2132.
 29. Aston LS, Seiber JN. 1996. Exchange of airborne organophosphorous pesticides with pine needles. *J Environ Sci Health B31*:671-698.
 30. Chan CH, Bruce G, Harrison B. 1994. Wet deposition of organochlorine pesticides and polychlorinated biphenyls to the Great Lakes. *J Great Lakes Res* 20:546-560.
 31. Blais JM, Schindler DW, Muir CGD, Kimpe LE, Donald DB, Rosenberg B. 1998. Accumulation of persistent organochlorine compounds in mountains of western Canada. *Nature* 395:585-587.
 32. Murphy TJ. 1981. Evaluation of a technique for measuring dry aerial deposition rates of DDT and PCB Residues. *Atmos Environ* 15:206-207.
 33. Safe S. 1993. Development of bioassays and approaches for the risk assessment of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin and related compounds. *Environ Health Perspect* 101:317-325.
 34. National Research Council. 1993. Estimating exposures. In *Pesticides in the Diets of Infants and Children*, National Academy Press, Washington, DC, USA, pp 137-156.
 35. Fujii Y, Asaka S. 1982. Metabolism of diazinon and diazoxon in fish liver preparation. *Bull Environ Contam Toxicol* 29:453-460.
 36. Keith LH. 1998. *Environmental Endocrine Disruptors: A Handbook of Property Data*. John Wiley & Sons, New York, NY, USA.
 37. Mayer FL, Ellersieck M. 1986. *Manual of Acute Toxicity: Interpretation and Data Base for 410 Chemicals and 66 Species of Freshwater Animals*. Resource Publication 160. U.S. Department of the Interior, Fish and Wildlife Service, Washington, DC.
 38. Sanders HO. 1972. The toxicities of some insecticides to four species of *Malacostracan crustacea*. Technical Report. Bureau of Sport Fish and Wildlife, Columbia, MO, USA.