DEPOSITION AND ACCUMULATION OF AIRBORNE ORGANIC CONTAMINANTS IN YOSEMITE NATIONAL PARK, CALIFORNIA

M. ALISA MAST,†† DAVID A. ALVAREZ,‡ and STEVEN D. ZAUGG§
†Colorado Water Science Center, U.S. Geological Survey, Denver, Colorado
‡Columbia Environmental Research Center, U.S. Geological Survey, Columbia, Missouri
§National Water Quality Laboratory, U.S. Geological Survey, Denver, Colorado

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Abstract—Deposition and accumulation of airborne organic contaminants in Yosemite National Park were examined by sampling atmospheric deposition, lichen, zooplankton, and lake sediment at different elevations. Passive samplers were deployed in high-elevation lakes to estimate surface-water concentrations. Detected compounds included current-use pesticides chlorpyrifos, daetal, and endosulfans and legacy compounds chlordane, dichlorodiphenyltrichloroethane-related compounds, dieldrin, hexachlorobenzene, and polychlorinated biphenyls. Concentrations in snow were similar among sites and showed little variation with elevation. Endosulfan concentrations in summer rain appeared to coincide with application rates in the San Joaquin Valley. More than 70% of annual pesticide inputs from atmospheric deposition occurred during the winter, largely because most precipitation falls as snow. Endosulfan and chlordane concentrations in lichen increased with elevation, indicating that mountain cold-trapping might be an important control on accumulation of these compounds. By contrast, chlorpyrifos concentrations were inversely correlated with elevation, indicating that distance from source areas was the dominant control. Sediment concentrations were inversely correlated with elevation, possibly because of the organic carbon content of sediments but also perhaps the greater mobility of organic contaminants at lower elevations. Surface-water concentrations inferred from passive samplers were at sub–parts-per-trillion concentrations, indicating minimal exposure to aquatic organisms from the water column. Concentrations in sediment generally were low, except for dichlorodiphenyltrichloroethane in Tenaya Lake, which exceeded sediment guidelines for protection of benthic organisms. Environ. Toxicol. Chem. 2012;31:524–533.

INTRODUCTION

Yosemite National Park is situated on the western slope of the Sierra Nevada in central California and is adjacent to the San Joaquin Valley, one of the most productive agricultural regions in the state. Each year, more than 30 million kilograms of pesticides are applied to agricultural fields in the valley (http://www.cdpr.ca.gov/). A portion of the pesticides may become airborne through volatilization and wind erosion during and after application [1]. The prevailing wind patterns in the valley, particularly during the summer months, transport airborne pesticides to the pristine mountain ecosystems of the Sierra Nevada [2], where they are likely to be deposited because of colder and wetter conditions at higher elevations [3,4]. Pesticide deposition in mountain ecosystems is of environmental concern, because these compounds tend to bioaccumulate in aquatic organisms and may pose a toxicological threat to sensitive species. High-elevation areas of the Sierra Nevada have experienced widespread declines in amphibian populations since the 1970s [5,6]. The most dramatic decline has been observed for the mountain yellow-legged frog (Rana muscosa), which has disappeared from more than 90% of its historic range in the Sierra Nevada [7]. Several hypotheses have been proposed to explain these declines, including the introduction of nonnative fish species [8], elevated levels of ultraviolet radiation [9], recent emergence of the chytrid disease [5], and increasing pesticide use in adjacent agricultural areas [10–12]. Davidson and Knapp [13] suggested that multiple stressors may be involved, although upwind pesticide application appears to have had the greatest influence on amphibian declines in the Sierras. Pesticides could directly affect amphibians if concentrations reach toxic levels. For example, chlorpyrifos and endosulfan, two commonly used insecticides in the San Joaquin Valley, were found to be highly toxic to two species of Sierran frogs at environmentally realistic concentrations in surface water [12]. Pesticides also might indirectly affect amphibians by compromising amphibian immune systems and making them more susceptible to disease such as the chytrid fungus [5].

Despite the role that pesticides may play in amphibian declines, relatively few studies have documented the distribution of organic contaminants in high-elevation areas of the Sierra Nevada. Several studies have reported pesticide concentrations in fish and amphibians [6,11,14–18], although measurements of pesticides in the atmosphere and aquatic habitats are relatively sparse. Pesticide concentrations in wet deposition [19] and in air, dry deposition, and surface water [2] were measured in Sequoia and Kings Canyon National Parks (Fig. 1), located in the Sierra Nevada near the southern end of the San Joaquin Valley. These parks periodically experience some of the worst air quality in the national park system (http://www.nps.gov/seki/naturescience/air.htm). Current-use and legacy pesticides in snow, air, water, conifer needles, lichen, sediment, and fish also were measured in Sequoia as one of eight core studies of national parks as part of the Western Airborne Contaminants Assessment Project (WACAP) [17]. Limited assessments of conifer needles, lichen, and air were...
also conducted in an additional 12 national parks, including Yosemite. The WACAP studies were conducted to determine the risk from airborne contaminants to remote park ecosystems in the western United States and Alaska. Other studies have investigated temporal and spatial patterns of pesticides in alpine lakes, air, and sediment in the southern Sierra Nevada to identify the relation between pesticide use and occurrence in remote mountain areas [18,20].

The purpose of the present study was to examine deposition and accumulation of airborne organic contaminants in Yosemite National Park from 2008 to 2009. The target analytes were 53 halogenated organic compounds, including current-use and historic-use pesticides and selected polychlorinated biphenyls (PCBs). Snow and rain samples were collected to determine which targeted organic contaminants are currently entering the park via atmospheric deposition and at what rates. Biomonitors (lichens) were used to investigate spatial patterns in the deposition of airborne contaminants. Finally, the occurrence and accumulation of organic contaminants in aquatic environments was examined using lake sediments and passive samplers. Most studies to date have focused on the area in and around Sequoia, and few studies have reported information for other high-elevation areas of the Sierra Nevada. The present study also differs from previous studies in that it includes rain and zooplankton and uses passive collectors for estimating concentrations in water. This information will improve our understanding of the processes responsible for organic contaminant distribution in the park and help to identify environments where contaminant effects would be most likely to occur.

MATERIALS AND METHODS

Study area description

Yosemite National Park is 3,080 km² in area and ranges in elevation from 600 m along the western boundary to over 4,000 m along the crest of the Sierra Nevada, which forms the eastern boundary (Supplemental Data, Fig. S1). Above 2,900 m, the park is dominated by large expanses of exposed bedrock and talus, with a sparse cover of lichens, grasses, and shrubs. Lower elevation areas (900–2,900 m) are dominated by extensive conifer forests. Mean annual precipitation increases considerably with elevation, ranging from 50 cm at lower elevations up to 150 cm in the alpine zone. More than 80% of annual precipitation falls as snow, which accumulates in a seasonal snowpack, which then melts in a large pulse in May and June. Approximately 95% of Yosemite is wilderness, and human activities are limited to tourism and recreation. Although the park is adjacent to large areas of undeveloped national forest lands, it is situated less than 50 km east of the San Joaquin Valley, which is one of the most productive agricultural regions in the state.

Sample collection

Snow samples were collected at 12 sites (S1–S12) during the spring of 2008 and 2009, just prior to snowmelt (Supplemental Data, Table S1 and Fig. S1). At each site, a snow pit was excavated, and temperature and density measurements were made along the exposed face. Complete vertical snow columns were collected from the snow pit face into 10-L Teflon® bags using precleaned polycarbonate scoops. The Teflon bags were closed with plastic cable ties and then wrapped in polypropylene bags for transport to the laboratory, where they were stored frozen until analysis.

Rain samples were collected during late spring and summer months at a site (B1) in Tuolumne Meadows during 2008 and 2009. The bulk (wet and dry) deposition collector consisted of a Teflon-coated stainless-steel funnel that drained into a 4-L brown glass bottle. Samples were collected at the site generally within 24 h of storm events, and any captured precipitation was
transferred to prebaked 1-L glass bottles. The funnel and collection bottle were replaced with clean equipment after each sample collection or once every two weeks if no precipitation occurred. Samples were then shipped on ice to the laboratory, where they were refrigerated until analysis. Daily precipitation amount was recorded at a collocated climate station in Tuolumne Meadows (http://cdec.water.ca.gov/cgi-progs/staMeta?station_id=TUM). Lichen samples were collected at 23 sites (V1–V23) during snow-free months in 2008 and 2009. The epiphytic lichen *Letharia vulpina* was selected for sampling because it grows on trees (hence it is not buried by winter snowpacks) and is distributed over a large elevation range. A limitation with this species is that it is not present in alpine areas of the park, so samples were collected only at elevations below 2,800 m. At each site, the target lichen was collected from at least eight different locations and composited into a single sample of approximately 40 g. Samples were obtained from tree branches or boles and placed into polyester bags. Samples were collected as clean and free from bark and other foreign material as possible. Nonpowdered vinyl gloves were worn to prevent contamination. Samples were placed in polyester bags, sealed with laboratory tape, and stored frozen until analysis.

Lake sediments were collected from 19 lakes (L1–L19) during the summer of 2008 and 2009. Because most lakes in Yosemite are situated at or above the treeline, little overlap existed in the spatial distribution of the lichen and lake sampling sites (Supplemental Data, Fig. S1). Sediment cores were collected by using a gravity benthos corer from a small inflatable raft anchored near the deepest point in each lake. The top 3 cm of sediment (surface) of each core was extruded from the core tube and transferred into a precleaned Teflon jar using a metal spatula. Sediment from three separate cores was combined into each jar to obtain sufficient sample mass (>100 g) for the pesticide analyses. A complete sediment core was collected at Tenaya Lake (L15) in 2009 and sectioned into intervals of 1 to 2 cm over a total length of 17 cm. Zooplankton samples were collected at eight of the lakes using a 150-mesh zooplankton net fitted to a Teflon collection jar. Horizontal tows behind the inflatable boat were required to obtain sufficient sample mass for the analysis. After collection, most water was drained from the collection jar and the sample was transferred to a precleaned Teflon jar. Sediment and zooplankton samples were kept cold during transport to the laboratory, where they were stored frozen until analysis.

A semipermeable membrane device (SPMD) is an integrative passive sampler designed to sample lipid- or fat-soluble semivolatile organic compounds (SOCs) from the water column (Supplemental Data, Table S2). Semipermeable membrane devices were utilized in the present study to estimate surface-water concentrations of SOCs for 10 high-elevation lakes in Yosemite. The SPMDs, which consist of a high-molecular-weight lipid encased in a nonporous membrane, were constructed at the U.S. Geological Survey, Columbia Environmental Research Center and enclosed in stainless-steel deployment canisters [21]. The prepared SPMDs were shipped in air-tight containers to field personnel at the park and stored frozen until they were deployed during June or July 2009. The deployed canisters were mounted on pedestals that suspended the SPMDs approximately 20 cm above the lake bottom. The pedestals were designed to be lightweight and easily assembled in the field to allow them to be backpacked to the remote sampling locations (Supplemental Data, Fig. S2). Mesh bags filled with sand and rocks collected at the sampling site were used to stabilize the pedestal on the lake bottom. The SPMD canisters were deployed in approximately 6 m of water and were tethered to a surface float for retrieval. Canisters were retrieved after 50 to 87 d and were transported from the field in air-tight containers and shipped on dry ice to the Columbia Environmental Research Center, where they were stored frozen until analysis.

**Analytical methods**

Snow, rain, lichen, sediment, and zooplankton samples were analyzed at the U.S. Geological Survey National Water Quality Laboratory in Lakewood, Colorado (http://nwwql.usgs.gov/), using methods described by S.D. Zaugg et al. (U.S. Geological Survey National Water Quality Laboratory, Denver, CO, unpublished manuscript). Frozen snow samples were melted at room temperature in the collection bags just prior to analysis. Analytes were extracted from melted snow and rain samples by passing 250 to 980 ml of unfiltered sample through disposable solid-phase extraction cartridges with 1-g chemically modified N-vinylpyrrolidone divinylbenzene resin (Water Oasis HLB cartridge; part No. 186000115). Solid samples (lichen, sediment, and zooplankton) were thawed just prior to processing and homogenized. Analytes were extracted from 1 to 2 g of lichen, 1 to 5 g of sediment (wet weight), and approximately 0.2 g of zooplankton using a pressurized liquid extraction system (Dionex ASE™ 200). The extraction was done at 2,000 psi for 30 min at 80°C, followed by 30 min at 200°C with a solvent mixture of 20% water:80% isopropyl alcohol. The organic compounds were isolated from the pressurized-liquid-extraction extracts using solid-phase-extraction cartridges with 1-g amino-propyl-based resin over 1-g chemically modified N-vinylpyrrolidone divinylbenzene resin. The solid-phase-extraction cartridges were dried with nitrogen, and the adsorbed compounds were eluted with 40 ml of a solvent mixture of 80% methylene chloride:20% diethyl ether through a sodium sulfate/Florisil solid-phase-extraction cartridge, then reduced in volume to approximately 1 ml under nitrogen gas. For the solid samples, a secondary extract cleanup was done by slowly drying the 1-ml extract onto an additional 1-g Florisil cartridge, which was eluted with 3 ml hexane, followed by 40 ml of a mixture of 94% pentane:6% acetone, and reduced to 1 ml. The extracts were analyzed by capillary-column gas chromatography/negative-chemical-ionization mass spectrometry for 53 halogenated compounds (Supplemental Data, Table S3). Reagent blanks, reagent spikes, and laboratory replicates were included with each analytical run of eight to 10 samples. In addition, each environmental and quality control sample was fortified with surrogate compounds before extraction to monitor performance of the sample-preparation process. The Supplemental Data include method detection limits and average spike recoveries for the target analytes (Supplemental Data, Tables S3 and S4) and surrogate recoveries for each environmental sample (Supplemental Data, Tables S5–S12). Concentrations of the target analytes reported in the tables are not corrected to the spike recoveries.

Semipermeable membrane device samples were analyzed at the Columbia Environmental Research Center for polycyclic aromatic hydrocarbons (PAHs) and selected organohalogen compounds, including chlorinated pesticides, total PCBs, polybrominated diphenyl ethers, and pyrethroid insecticides. Semipermeable membrane device samples also were screened using the yeast estrogen screen for the total estrogenicity of sampled chemicals, which can be an indicator of endocrine disruption in aquatic organisms [22]. Details of SPMD construction,
processing, analysis, and estimations of water concentrations are given in the Supplemental Data.

Field quality control

Seven blanks were prepared by pouring commercially available (B&J brand) pesticide-grade organic blank water over the sampling equipment into the collection vessel either in the laboratory (equipment blank) or in the field (field blank; Supplemental Data, Table S5). Most compounds generally were not detected or were detected at concentrations that would not affect data analysis. Dacthal was detected at concentrations of about 1 ng/L in the rain collector blanks in 2008. However, these concentrations were two orders of magnitude lower than in rain, indicating that the contamination likely did not bias concentrations in the environmental samples. Four field replicates were collected for precipitation (snow and rain), and five were collected for solid samples (lichen, sediment, and zooplankton; Supplemental Data, Table S6). Field quality control for SPMD samples included deployment of replicate samplers at two lakes and a single composite trip blank, which was carried to each lake and opened to the air during canister deployment and retrieval. The target compounds were not detected in the composite trip blank.

RESULTS AND DISCUSSION

Concentrations in snow

Atmospheric inputs during the winter were characterized using full-depth snowpack samples collected just prior to the beginning of snowmelt (March), which should represent the majority of wet and dry deposition for the winter snowfall period. Snow concentrations for the 13 samples collected are summarized in Supplemental Data, Table S7, and in Figure 2A. Current-use pesticides detected were chlorpyrifos, dacthal, endosulfan isomers I and II, endosulfan sulfate, and trifluralin. Chlorpyrifos was detected in 100% of samples at concentrations ranging from 0.14 to 4.9 ng/L. Chlorpyrifos is an organophosphate insecticide that is widely used in the San Joaquin Valley (Fig. 1), with greatest usage from May through August (http://calpip.cdpr.ca.gov/main.cfm). Dacthal was also detected in 100% of snow samples at concentrations ranging from 1.2 to 5.8 ng/L. Dacthal is a pre-emergence herbicide applied primarily in winter and again in late summer and fall but is not widely used in the San Joaquin Valley (Fig. 1). However, dacthal is heavily used year-round in the coastal valleys of central California west of the San Joaquin Valley. Endosulfan I and II were detected in 100% of samples (range 0.15–2.1 ng/L) and endosulfan sulfate, which is a degradation product of endosulfan, was detected in 85% of samples (range 0.06–1.5 ng/L). Endosulfan is the only chlorinated cyclodiene insecticide still in use in the United States. However, concern is growing about the persistence and toxicity in the environment, and agricultural use in the United States is being phased out (http://www.epa.gov/pesticides/eregistration/endosulfan/endosulfan-cancel-fs.html). Despite much lower application rates of dacthal and endosulfans compared with chlorpyrifos, concentrations in snow were similar among the three pesticides (Fig. 2A). Snow concentrations of current-use pesticides in Yosemite were comparable to those reported for snow in nearby Sequoia [23] but much higher than in snow from the Rocky Mountains, particularly for chlorpyrifos [23,24]. For example, mean concentrations of chlorpyrifos in Yosemite (1.8 ng/L) and Sequoia (2.3 ng/L) were more than an order of magnitude higher than in national parks in Colorado (0.03 ng/L) and Montana (0.07 ng/L) [23,24], which likely reflects higher application rates in the San Joaquin Valley. In an earlier study in Sequoia, chlorpyrifos and endosulfans were also detected in snow as well as chlorothalonil, diazinon, and malathion [19], which were not included in the present study.

The legacy pesticides detected in snow included two chlordane components, trans-chlordane and trans-nonachlor, and dieldrin. Chlordane was used as an agricultural insecticide from 1948 to 1978 and then for termite control until 1988, and dieldrin was used as a termiticide and was banned from use in the United States in 1974. Because these compounds have not been used in the United States for several decades, their presence indicates that they continue to be volatilized, probably from previously contaminated soils, and transported to remote areas [23]. Detected concentrations of legacy pesticides ranged from 0.05 to 0.35 ng/L for chlordanes and 0.12 to 0.19 ng/L for dieldrin and were much lower than concentrations for current-use pesticides. Hageman et al. [23] reported several legacy pesticides in snow from Sequoia, including dieldrin, lindane (γ-HCH), chlordanes, and hexachlorobenzene. Lindane and hexachlorobenzene were not detected in Yosemite, and dieldrin

![Fig. 2. Distribution of detected pesticide concentrations in snow and rain (A), lichen (B), and lake sediment (C). For the box-and-whisker plots, the box represents the interquartile range, and the center line is the median; box whiskers are 1.5 times the interquartile range, and points are outliers. Endo = sum of endosulfans; Chpy = chlorpyrifos; Dact = dacthal; DDT = dichlorodiphenyldichloroethane and related compounds dichlorodiphenyltrichloroethane and dichlorodiphenyldichloroethylene; Chor = sum of chlordanes; HCB = hexachlorobenzene; Diel = dieldrin.](Image)
concentrations in Yosemite were an order of magnitude lower than mean concentrations (1.8 ng/L) reported for Sequoia [23]. Polychlorinated biphenyls were also reported in Sequoia snow but were not detected in any Yosemite snow samples.

Concentrations in rain

Although most of the annual precipitation to high-elevation areas of Yosemite occurs as snow during winter months, significant pesticide deposition may occur in rain during the spring and summer, because this is the period of greatest pesticide usage. Results for the rain collector operated in Tuolumne Meadows during the snow-free season in 2008 to 2009 are provided in Supplemental Data, Table S8, and summarized in Supplemental Data, Figure 2A. Similarly to the case for snow, the most frequently detected current-use pesticides in rain were chlorpyrifos, dacthal, and endosulfans. Concentrations among rain samples were fairly similar to each other, with the exception of the two samples collected in July, 2008 (Supplemental Data, Table S8). These samples were collected after a six-week dry period during which only 1 cm of rain fell at the site. These two samples had no detectable chlorpyrifos but very high concentrations of dacthal (169 and 217 ng/L) and endosulfan I (117 and 274 ng/L). In addition, the samples had elevated concentrations of dieldrin (5.2 and 12 ng/L) and trans-nonachlor (3.3 and 4.8 ng/L), and a few PCB congeners were detected. One possible explanation for the elevated pesticide concentrations in 2008 is that organic contaminants accumulated in the atmosphere during the dry period in June and early July. The absence of chlorpyrifos was somewhat unexpected considering that application rates are highest in June and that the other pesticides were found in elevated concentrations. This may indicate that, during the drought period, chlorpyrifos was degraded in the atmosphere because of the warm temperatures and sunlight. Air concentrations of chlorpyrifos oxon in the Sierra Nevada have been reported to be higher than chlorpyrifos during the summer because of atmospheric oxidation [2]. Chlorpyrifos oxon or other degradates were not measured in the present study, so the deposition of chlorpyrifos degradates cannot be quantified for Yosemite.

During June and July of 2009, which had average rainfall, chlorpyrifos was detected in several rain samples but at concentrations typically lower than those detected in snow, which is consistent with the hypothesis of greater degradation during the summer because of increased sunlight and oxidants in the air [2]. In contrast to chlorpyrifos, dacthal concentrations in rain during 2009 were approximately four times higher than in snow, despite the fact that application occurs year-round. This could reflect higher air concentrations of current-use pesticides during warmer months because of volatilization and/or greater scavenging by rain than snow [25]. In addition, dacthal has a much longer atmospheric half-life (24 d) than many current-use pesticides (<1 d), suggesting that long-range transport could be an important source for this pesticide [26].

Because little precipitation occurs in the Sierra Nevada during the summer, few reports of pesticides in summer deposition have been published. LeNoir et al. [2] measured pesticides in air and dry deposition during the summer for sites in Sequoia and detected the same compounds found in rain from Yosemite as well as diazinon and malathion, which were not measured in the present study. The herbicide atrazine was frequently detected in rain at a high-elevation site in the Rocky Mountains [24]. Atrazine was not detected in any samples from Yosemite or Sequoia [2,19], which likely reflects low application rates in the San Joaquin Valley (<50 kg annually).

Relatively frequent summer precipitation in 2009 allowed investigation of temporal patterns in pesticide deposition. Total endosulfans in rain showed a seasonal pattern of decreasing concentrations in spring and increasing concentrations in summer (Fig. 3A). Monthly application rates (2009) for endosulfan in the San Joaquin Valley showed a similar pattern, with a minimum during April and May, approximately the same time as minimum concentrations in precipitation. Bradford et al. [20] reported similar correspondence between seasonal endosulfan concentrations in alpine lakes in the Sierra Nevada and endosulfan application rates. Back-trajectory analysis indicated that most of the endosulfan reaching the lakes originated in localized upwind areas in the San Joaquin Valley [20]. Dacthal concentrations in precipitation did not exhibit any temporal pattern other than the high concentration in March (Fig. 3B). Dacthal application rates were low during spring and increased in late summer, showing little correspondence with concentrations in precipitation. Bradford et al. [20] found a similar lack of correspondence between lake-water concentrations and application rates and suggested that dacthal may originate from more distant sources. Indeed, dacthal use is heavy throughout the year in coastal valleys of central California to the west of the San Joaquin Valley.

Atmospheric deposition rates

Annual deposition rates were estimated for dacthal, total endosulfans (I + II + sulfate), chlorpyrifos, and dieldrin by combining results from snow and rain. Winter and summer deposition rates were computed for 2009 based on daily
precipitation amount from the climate station in Tuolumne Meadows. Winter precipitation was summed over the months of October through March and multiplied by average snow concentrations to obtain deposition for the winter period. Concentrations for undetected compounds were set equal to one-half the analytical reporting limit. Deposition during snow-free months (April–September) was calculated by multiplying the concentrations in each sample by the precipitation amount over the sampling period. Results are presented in Table 1, including estimates for Sequoia from 2003 to 2005 [17]. In Yosemite, more than 70% of pesticide deposition occurred during the winter, largely because precipitation is dominated by snowfall at high elevations in the Sierra Nevada. Only dacthal had higher deposition during the summer months, reflecting higher concentrations in rain compared with snow. Winter deposition rates in Yosemite were similar to those reported for Sequoia, with the exception of dieldrin, which was substantially higher in Sequoia. Deposition rates of chlorpyrifos were lower than the other current-use pesticides despite high application rates in the valley. Summer deposition rates in the present study may be underestimated because they do not include the chlorpyrifos oxon degrade.

Concentrations in lichen

Biomonitoring is another method used in air-quality assessments of remote areas [27]. Commonly used biomonitors include lichens, pine needles, and mosses; however lichens have an advantage because they have a larger intercepting area than other biomonitors, and they absorb all pollutants directly from the atmosphere [28]. In Yosemite, dacthal and endosulfans were the dominant current-use pesticides in lichens and were detected in 100% of samples (Supplemental Data, Table S9). Dry-weight concentrations of dacthal ranged from 1.9 to 26 ng/g, and total endosulfans ranged from 2.0 to 34 ng/g. Other current-use pesticides detected were chlorpyrifos (70% of samples) and the degrade pentachloroanisolide (22%). The average lipid content of lichens was approximately 5%, indicating that lipid-normalized concentrations would be approximately 20 times higher than dry-weight concentrations. Detected legacy pesticides included total chlordanes (83% of samples), hexachlorobenzene (87%), and dieldrin (22%). Among the dichlorodiphenyltrichloroethane (DDT)-related compounds, the degrade dichlorodiphenyldichloroethylene (DDE) was detected in only one sample. Lichens had more detections of legacy compounds relative to rain or snow, perhaps because compounds with high lipid solubility favor adsorption on organic matter (Fig. 2B). In addition, because lichens do not regularly shed leaves or needles, they can potentially accumulate contaminants over many years.

Published pesticide data for lichens in high-elevation areas are limited. Pesticide concentrations in the present study were similar to those measured in Sequoia by the WACP study [17]. Average concentrations for the same species in Sequoia collected from 2003 to 2004 were 0.92 ng/g for chlorpyrifos, 8.0 ng/g for dacthal, 23 ng/g for total endosulfans, and 0.95 ng/g for total chlordanes. By comparison, average concentrations in the present study were 1.7 ng/g for chlorpyrifos, 9.2 ng/g for dacthal, 13.3 ng/g for total endosulfans, and 0.75 ng/g for total chlordanes. The Sequoia lichens collected by WACP commonly had detections of lindane (0.22–1.1 ng/g) and DDT-related compounds (2.0–11 ng/g), which were not detected in the Yosemite samples (except for one detection of DDE). The reason for the lack of lindane detections in the present study is not clear but might be related to differences in the analytical methods between the two studies, such as differences in sample size, cleanup procedures, or analytical sensitivity. Pesticide concentrations also have been reported for lichens collected in mountainous areas of western Canada [29]. Concentrations in the Canadian samples were similar for endosulfan (3.1–21 ng/g), but slightly lower for total chlordanes (0.01–0.06 ng/g). Lindane (γ-HCH) was also detected in all Canadian lichens (0.17–0.97 ng/g) as well as α-HCH (0.14–3.8 ng/g), which was not included in the present study.

Concentrations in lake sediment

The detected current-use pesticides in sediment were chlorpyrifos, dacthal, and the endosulfan isomers (Fig. 2C and Supplemental Data, Table S10). Chlorpyrifos was detected in two and dacthal was detected in eight of the 19 sediment samples, which contrasts with snow, in which it was detected in all samples. The degradation product endosulfan sulfate was the most frequently detected endosulfan component in sediment, in contrast to snow, in which the isomer forms were dominant. Endosulfan sulfate typically is more persistent in aqueous environments than either of the parent isomers [30]. Among the legacy pesticides, chlordane components (cis-chlordane, trans-chlordane, cis-nonachlor, and trans-nonachlor) were most frequently detected, with 95% of samples having detections of at least one component. Dichlorodiphenylchloroethylene, a degradation product of DDT, was detected in 68% of sediments in concentrations ranging from 1.6 to 21 ng/g, which were the highest of any detected pesticide. Several PCB congeners (industrial compounds) were also detected, although individual concentrations were very low (0.44 ng/g or less). Sediment results for Yosemite compare closely with current use and legacy compounds detected in surface sediment collected from 28 shallow ponds in Sequoia [18]. The same general suite of

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Table 1. Winter and summer deposition rates of pesticides in Yosemite National Park (CA, USA) for 2009 and winter deposition in Sequoia National Park (CA, USA) from 2003 to 2005

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*Winter estimates from the Western Airborne Contaminants Assessment Project study [24].
compounds was detected in zooplankton samples collected from a subset of the lakes (Supplemental Data, Table S11).

Historical changes in pesticide deposition were investigated by using a sediment core collected at Tenaya Lake (Supplemental Data, Table S12). Profiles of pesticide concentrations as a function of sediment depth showed pesticides only in the top 5 cm of the core (Fig. 4). Concentrations of DDT-related compounds and chlordane peaked at the 2- to 3-cm depth, then generally decreased toward the surface, reflecting discontinued usage of the compounds for several decades. Although the sediment profile was not age dated, the concentration pattern can be compared with a dated core collected in Sequoia [17], which indicated the first occurrence of pesticides in the late 1950s and the peak in dichlorodiphenyldichloroethane (DDD) around 1961. Dichlorodiphenyldichloroethane concentrations in the Sequoia core were also elevated in subsurface sediments from a subset of the lakes (Supplemental Data, Table S11). Most detections were less than the method quantitation limit (see Supplemental Data), and the associated estimated (E) concentrations (though not compound identification) have a greater uncertainty than concentrations greater than the method quantitation limit. Endosulfan I was the only compound detected at concentrations greater than the method quantitation limit in all samples.

A few of the commonly identified PAHs were found in the SPMD samples (Supplemental Data, Table S14), including naphthalene, phenanthrene, fluoranthene, and pyrene (PAHs were not analyzed in the other sample media). The PAHs that were detected are ones that have a higher volatility and are commonly identified in air and water samples [33,34]. Losses of the photolysis marker (loss in sampler because of exposure to sunlight) ranging from 55 to 88% at Lower McCabe Lake, Ostrander Lake, and Upper Granite Lake indicate that PAHs may have been present at higher concentrations than measured by the SPMD; however, it is reasonable to assume that any PAHs present in the water column had also photolyzed, just as the ones inside the SPMD did. It should be noted that the photolysis products of many PAHs have a higher aquatic toxicity than the parent molecules [35]. Polycyclic aromatic hydrocarbons are a large group of chemical compounds found naturally, for example, in oil and coal. Polycyclic aromatic hydrocarbons are also emitted to the environment as the result of human activities, particularly from the incomplete combustion of fossil fuels and the burning of wood. Emissions of PAHs can be transported long distances in the atmosphere, contaminating remote regions far from the source of pollution. The wide distribution of PAHs is of concern, because the compounds can persist in the environment and have toxic and carcinogenic properties that can affect a variety of organisms [22].

Estrogenicity was not measurable in samples from any of the field-deployed or quality-controlled SPMDs. However, this does not rule out the possibility of estrogenic chemicals being present in the lakes. Many estrogenic chemicals tend to contain polar functional groups and have higher water solubilities (log octanol–water partition coefficients <4) and therefore are not readily sampled by the SPMD, which preferentially samples neutral, hydrophobic chemicals [21].
Results for the SPMD samples indicate that organic contaminants are present in aquatic environments of Yosemite, but generally at very low levels. Estimated lake-water concentrations were at sub-parts-per-trillion levels and were orders of magnitude below aquatic-life benchmarks (http://www.epa.gov/oppefed1/ecorisk_ders/aquatic_life_benchmark.htm), indicating minimal exposure to aquatic life from the water column, at least during the months when the SPMDs were deployed. Exposure may be greater during snowmelt, when pesticides accumulated in the snowpack are released to surface waters. To characterize the degree of exposure better, SPMDs would have to be deployed in April and May to capture the start of the snowmelt pulse, when concentrations would likely be highest.

Elevation gradients in pesticide concentrations

Numerous studies have reported concentration gradients of organic contaminants in mountain environments that increase with increasing elevation, a process termed "mountain cold-trapping" [4,36,37]. It has been proposed that this process is controlled largely by the temperature dependence of organic vapor partitioning into rain, snow, and aerosols [38]. A relation between pesticide concentrations and site elevation was not apparent for the snowpack samples collected in the present study. Cold-trapping of organic compounds in mountain snowpacks has been documented in only one study, which was conducted in the Canadian Rockies [4]. The lack of an elevation trend in Yosemite may reflect the relatively narrow elevation range (~700 m) over which snowpack samples were collected compared with the Canadian study, which spanned a range of 2,330 m. In addition, the compounds most frequently detected in the present study were not predicted as those most subject to cold-trapping in midlatitude mountains [38].

In contrast to snow, concentrations in lichens from Yosemite exhibited statistically significant correlations with elevation for some pesticides (Fig. 5A,C). Dacthal ($r^2 = 0.08, p = 0.09$), total endosulfans ($r^2 = 0.63, p < 0.001$), and total chlordanes ($r^2 = 0.33, p = 0.01$) showed positive correlations with elevation, and chlorpyrifos showed an inverse correlation ($r^2 = 0.44, p < 0.001$). Correlations between organic contaminants in vegetation and elevation have been reported for lichen in other western national parks [17] (data for Sequoia included in Fig. 5A,C) and for conifer needles and lichens in western Canada [36]. Because of strong temperature gradients along mountain slopes, positive pesticide gradients suggest that accumulation of some compounds on lichens is controlled by an increase in the foliage–air partitioning coefficient at lower temperatures [36]. The degree to which certain compounds accumulate depends on the relative volatilities of the compounds, with the more volatile compounds showing greater accumulation at higher elevations [29].

The inverse relation between chlorpyrifos and elevation may indicate that distance from source areas is more important than air–foliage partitioning in controlling the distribution of chlorpyrifos in the park [18]. Decreasing concentrations with
distance from source areas typically result from dilution, dispersion, and degradation [38]. For pesticides derived from the San Joaquin Valley, greater deposition and exposure would be expected to occur at the lowest elevations in Yosemite, because these sites are farther west and closer to agricultural areas. In fact, when correlated with distance from the San Joaquin Valley, chlorpyrifos concentrations showed a substantially stronger correlation than with elevation (Fig. 5D). A tracer study conducted in the San Joaquin Valley [39] showed that air is transported from the valley into the Sierra Nevada by diurnal upslope flows during the summer, with tracer levels decreasing with increasing distance and elevation from the valley floor, which is consistent with the chlorpyrifos results for Yosemite. In contrast, endosulfan concentrations, which likely are controlled by temperature, showed a much weaker correlation with distance than with elevation (Fig. 5B). The relation between chlorpyrifos and distance (Fig. 5D) appeared to level out above 90 km, which is at an elevation approaching the treeline (3,000 m). A similar result was reported by Bradford et al. [18], who found little relation between pesticide concentrations and distance from the San Joaquin Valley for sites above 2,800 m. It was suggested that transport processes had less influence on concentration variability in the alpine zone than at lower elevations in the Sierra Nevada [18].

Pesticides in lake sediment and SPMD samples also showed elevational gradients in the park. Total chlordane concentrations in sediment exhibited an inverse correlation with lake elevation ($r^2 = 0.75$, $p < 0.001$), as did endosulfan sulfate ($r^2 = 0.55$, $p < 0.001$). A stronger relation was found when all the pesticide concentrations were summed ($r^2 = 0.83$, $p < 0.001$; Fig. 6). Interestingly, the SPMD samples also showed a significantly negative relation with elevation for endosulfan sulfate ($r^2 = 0.87$, $p < 0.001$; Fig. 6). One possible explanation is that concentrations of pesticides in sediment are controlled by the organic carbon content of the sediment, which increases pesticide concentrations in the sediment because of greater adsorption of hydrophobic compounds. The organic carbon content of sediments was inversely correlated with elevation ($r^2 = 0.61$, $p < 0.001$). However, after the concentrations had been normalized to carbon content, an inverse relation with total pesticide concentrations in sediment and elevation was still evident, although weaker ($r^2 = 0.39$, $p = 0.005$), suggesting that carbon content alone does not explain the elevation gradient. Little evidence exists that the pesticide sediment trend reflects deposition patterns in the park, because precipitation amount and dry deposition (inferred from lichen data) both increase with elevation (chlorpyrifos excluded). Another possibility is that the inverse sediment trend with elevation might reflect enhanced mobility of pesticides in aquatic systems at lower elevations because of greater soil cover and organic matter in watersheds at lower elevations in the park.

SUPPLEMENTAL DATA

Figs. S1–S2.

TABLES S1–S14.

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