

# **Organochlorine Compounds and Current-Use Pesticides in Snow and Lake Sediment in Rocky Mountain National Park, Colorado, and Glacier National Park, Montana, 2002–03**

By M. Alisa Mast, William T. Foreman, and Serena V. Skaates

Prepared in cooperation with the  
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## Conversion Factors

### SI to Inch/Pound

Multiply	By	To obtain
Length		
centimeter (cm)	0.3937	inch (in)
meter (m)	3.281	foot (ft)
kilometer (km)	0.6214	mile (mi)
Area		
square meter (m <sup>2</sup> )	0.0002471	acre
hectare (ha)	2.471	acre
square kilometer (km <sup>2</sup> )	247.1	acre
square meter (m <sup>2</sup> )	10.76	square foot (ft <sup>2</sup> )
hectare (ha)	0.003861	square mile (mi <sup>2</sup> )
square kilometer (km <sup>2</sup> )	0.3861	square mile (mi <sup>2</sup> )
Volume		
liter (L)	33.82	ounce, fluid (fl. oz)
liter (L)	2.113	pint (pt)
liter (L)	1.057	quart (qt)
liter (L)	0.2642	gallon (gal)
cubic meter (m <sup>3</sup> )	264.2	gallon (gal)
cubic meter (m <sup>3</sup> )	0.0008107	acre-foot (acre-ft)
Mass		
milligram (mg)	$0.03527 \times 10^{-3}$	ounce, avoirdupois (oz)
gram (g)	0.03527	ounce, avoirdupois (oz)
microgram	$0.03527 \times 10^{-6}$	ounce, avoirdupois (oz)
kilogram (kg)	2.205	ounce, avoirdupois (lb)
nanogram (ng)	$0.03527 \times 10^{-9}$	ounce, avoirdupois (oz)
dalton	$0.058 \times 10^{-24}$	ounce, avoirdupois (oz)
Pressure		
pascal (Pa)	9.869	atmosphere, standard (atm)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:  
 $^{\circ}\text{F}=(1.8\times^{\circ}\text{C})+32$

Vertical coordinate information is referenced to the North American Vertical Datum of 1988 (NAVD 88).

Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83).

Altitude, as used in this report, refers to distance above the vertical datum.

## Abbreviations

cm, centimeter  
km, kilometer  
kPa, kilopascal  
L, liter  
m, meter  
mL, milliliter  
mm, millimeter  
min, minutes  
ng/L, nanogram per liter  
 $\mu\text{g}/\text{kg}$ , microgram per kilogram  
 $\mu\text{g}/\text{L}$ , microgram per liter  
 $\mu\text{g}/\text{m}^2$ , microgram per square meter  
 $\mu\text{m}$ , micrometer  
°C, degrees Celsius

## Acronyms

$\alpha$ -HCH-*d6*, alpha-hexachlorocyclohexane-*d6*  
CRM, certified reference material  
CUP, current-use pesticides  
DCM, dichloromethane  
DDD, *p,p'*-dichlorodiphenyldichloroethane  
DDE, *p,p'*-dichlorodiphenyldichloroethene  
DDT, *p,p'*-dichlorodiphenyltrichloroethane  
E, estimated concentration  
GC, gas chromatography  
GC/ECD, gas chromatography with electron-capture detection  
GC/EIMS, gas chromatography with electron-impact mass spectrometry  
GC/ECNIMS, gas chromatography with electron capture negative ion mass spectrometry  
GLAC, Glacier National Park  
HCB, hexachlorobenzene  
HCH, hexachlorocyclohexane  
MRL, method reporting limit

NAWQA, National Water-Quality Assessment Program  
NPS, National Park Service  
NWQL, National Water Quality Laboratory  
OCC, organochlorine compounds  
OHC, organohalogen compounds  
PAH, polycyclic aromatic hydrocarbons  
PCB, polychlorinated biphenyls  
PBDE, polybrominated diphenyl ethers  
PTFE, polytetrafluoroethylene  
RPD, relative percent difference  
ROMO, Rocky Mountain National Park  
SNOTEL, Snow Telemetry  
USGS, U.S. Geological Survey  
WACAP, Western Air Contaminants Assessment Project

# Organochlorine Compounds and Current-Use Pesticides in Snow and Lake Sediment in Rocky Mountain National Park in Colorado and Glacier National Park in Montana, 2002–03

By M. Alisa Mast, William T. Foreman, and Serena V. Skaates

## Abstract

Organochlorine compounds and current-use pesticides were measured in snow and lake-sediment samples from Rocky Mountain National Park in Colorado and Glacier National Park in Montana to determine their occurrence and distribution in high-elevation aquatic ecosystems. The U.S. Geological Survey, in cooperation with the National Park Service, collected snow samples at eight sites in Rocky Mountain National Park and at eight sites in Glacier National Park during spring of 2002 and 2003 just prior to the start of snowmelt. Surface sediments were collected from 11 lakes in Rocky Mountain National Park and 10 lakes in Glacier National Park during summer months of 2002 and 2003. Samples were analyzed for organochlorine compounds by gas chromatography with electron-capture detection and current-use pesticides by gas chromatography with electron-impact mass spectrometry. A subset of samples was reanalyzed using a third instrumental technique (gas chromatography with electron-capture negative ion mass spectrometry) to verify detected concentrations in the initial analysis and to investigate the presence of additional compounds.

For the snow samples, the pesticides most frequently detected were endosulfan, dacthal, and chlorothalonil, all of which are chlorinated pesticides that currently are registered for use in North America. Concentrations of these pesticides in snow were very low, ranging from 0.07 to 2.36 nanograms per liter. Of the historical-use pesticides, hexachlorobenzene, dieldrin, and *trans*-nonachlor were detected in snow but only in one sample each. Annual deposition rates of dacthal, endosulfan, and chlorothalonil were estimated at 0.7 to 3.0 micrograms per square meter. These estimates are likely biased low because they do not account for pesticide deposition during summer months.

For the lake-sediment samples, DDE (*p,p'*-dichlorodiphenyldichloroethene) and DDD (*p,p'*-dichlorodiphenyldichloroethane) were the most frequently detected

organochlorine compounds. DDE and DDD are degradation products of DDT (*p,p'*-dichlorodiphenyltrichloroethane), which is a well-documented, persistent organochlorine insecticide that has been banned from use in the United States since 1972. Detected concentrations were very low, ranging from 0.12 to 4.7 micrograms per kilogram, and probably pose little threat to aquatic organisms in park lakes. DDD and DDE concentrations in a sediment core from Mills Lake in Rocky Mountain National Park indicate that atmospheric deposition of DDT and possibly other banned organochlorine compounds to high-elevation parks has been in decline since the 1970s. Commonly detected current-use pesticides in lake sediments included dacthal and endosulfan sulfate, which ranged in concentrations from 0.11 to 0.26 micrograms per kilogram for dacthal and 0.12 to 1.2 micrograms per kilogram for endosulfan sulfate. Both compounds were found in nearly all the snow samples, confirming that some current-use pesticides entering high-elevation aquatic ecosystems through atmospheric deposition are accumulating in lake sediments and potentially in aquatic biota.

## Introduction

A number of studies have documented the presence of organochlorine compounds in remote polar ecosystems (Simonich and Hites, 1995; Wania and Mackay, 1996; Blais, 2005). These compounds are accumulating at high latitudes due to long-range atmospheric transport and the effects of cold condensation, a process which causes semivolatile organic compounds used at warmer temperate latitudes to accumulate in colder high-latitude regions (Simonich and Hites, 1995). Organochlorine compounds frequently detected in these environments include the pesticides DDT, hexachlorocyclohexanes ( $\alpha$ - and  $\gamma$ -HCH), and hexachlorobenzene (HCB), and the industrially used polychlorinated



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biphenyls (PCB). Although usage of most of these compounds ceased in the 1970s and 1980s, they are still detected in the environment because of their resistance to natural degradation processes (Majewski and Capel, 1995). These compounds are of environmental concern because they tend to concentrate in aquatic organisms through bioconcentration and biomagnification and, for some, are known or suspected of disrupting the endocrine system of aquatic organisms. Several recent studies also have documented the accumulation of organochlorine compounds in high-elevation areas at temperate latitudes (Blais and others, 1998; Carrera and others, 2001; Grimalt and others, 2001; Blais, 2005; Daly and Wania, 2005; Wilkinson and others, 2005). Blais and others (1998) detected organochlorine compounds in seasonal snowpacks in Canada and found that concentrations tended to increase with increasing elevation. Grimalt and others (2001) reported elevated concentrations of organochlorine compounds in lake sediment and fish tissue in mountainous areas of Europe. The authors hypothesized that low annual air temperature at high elevations was causing selective accumulation of organochlorine compounds in temperate mountain areas. Based on these results, it has been suggested that temperate mountains in the Western United States, such as the Rocky Mountains, Cascade Range, and Sierra Nevada, may be particularly susceptible to accumulation of organochlorine compounds because they have low annual air temperatures, relatively high rates of precipitation, and are close to agricultural and urban source areas.

Although the widespread occurrence of organochlorine compounds in the environment has been documented, much less is known about long-range atmospheric transport of current-use pesticides and the persistence of these compounds in aquatic environments, particularly in remote mountainous areas. A major class of current-use pesticides is organophosphate insecticides, which includes pesticides such as chlorpyrifos, malathion, and diazinon and accounts for about 65 percent of insecticide usage in the United States (Majewski and Capel, 1995). The triazine and acetanilide herbicides, which include atrazine and metolachlor, account for about 50 percent of herbicide usage in the United States (Majewski and Capel, 1995). Current-use pesticides have been detected in precipitation collected in remote areas of the United States indicating these compounds can be transported by air currents over substantial distances (Goolsby and others, 1995; Majewski and Capel, 1995; McConnell and others, 1998; Mast and others, 2003). McConnell and others (1998) detected several organophosphate insecticides in rain and snow samples collected at high elevations in the Sierra Nevada of California. Atmospheric transport of pesticides from California's Central Valley, one of the heaviest pesticide-use areas in the United States, was considered the most likely source of the pesticides. These compounds also were detected in surface-water samples from two areas in the Sierra Nevada but not in frog tissue

(Fellers and others, 2004), indicating the organophosphate insecticides may not be as easily accumulated in aquatic ecosystems as organochlorine compounds (Majewski and Capel, 1995). Mast and others (2003) detected the current-use pesticides atrazine, carbaryl, and dacthal in rain samples collected at a high-elevation site in the Colorado Front Range. The authors suggested a likely source of these pesticides was urban and agricultural areas on the eastern plains of Colorado.

National Parks in mountainous areas of the Western United States have a large percentage of lakes and streams at high elevations that may be at risk from long-range transport and deposition of organochlorine compounds and current-use pesticides. To date only a few measurements have been made in high-elevation parks (Heit and others, 1984; Tate and Heiny, 1996; Stephens and Deacon, 1997; Cubala and others, 1995; McConnell and others, 1998; Mast and others, 2003) so relatively little is known about deposition to and occurrence in these sensitive ecosystems. The U.S. Geological Survey (USGS), in cooperation with the National Park Service (NPS), conducted a study in 2002–03 to provide baseline information on organic contaminants at two National Parks in the Rocky Mountain Region. This information is needed by park managers to protect and preserve park resources from damage by atmospheric contaminants as required by the Clean Air Act Amendments of 1977 (<http://www2.nature.nps.gov/air/regs/cleanAir.cfm>, accessed January 2006).

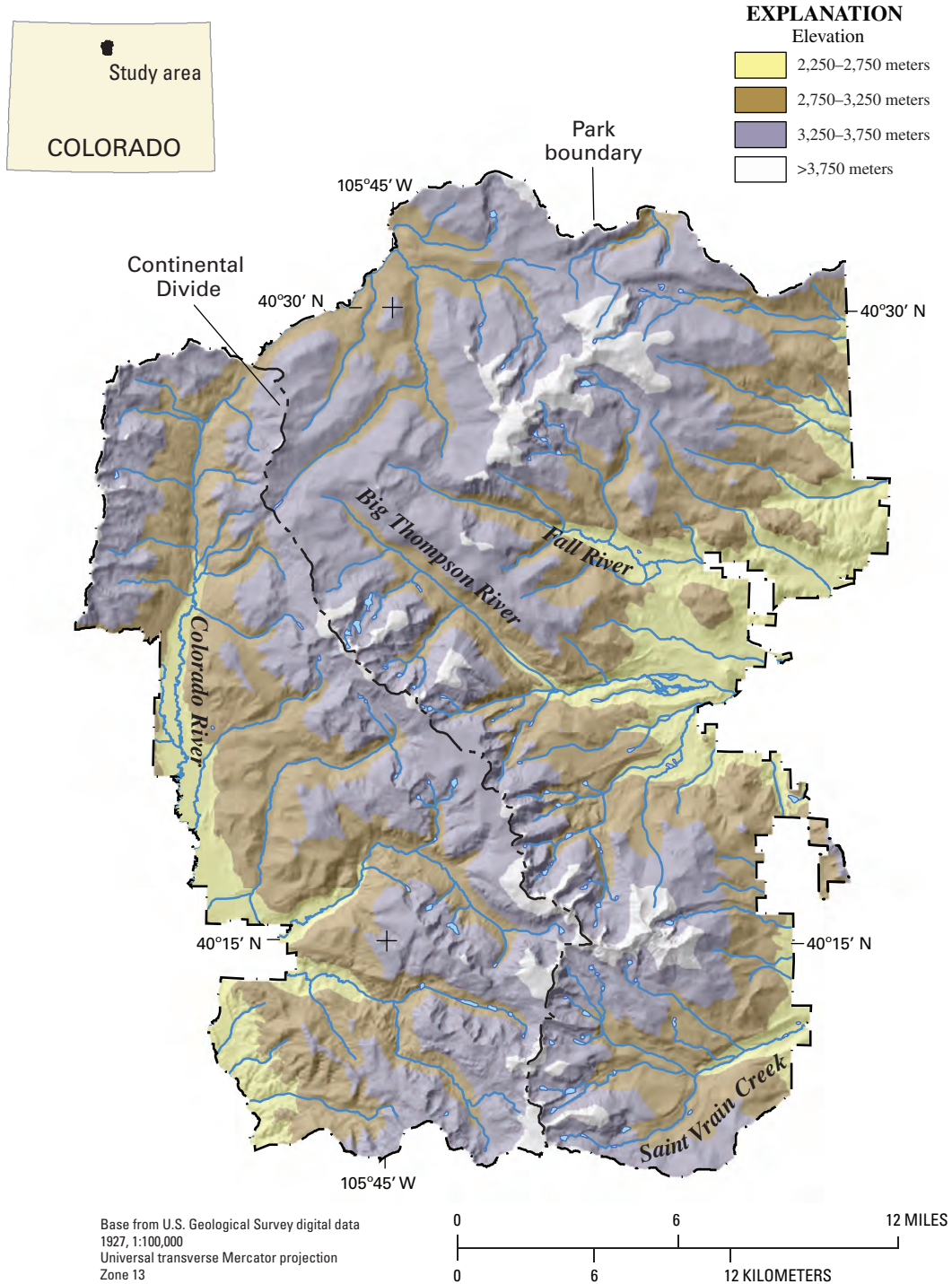
### Purpose and Scope

The purpose of this report is to describe the occurrence and distribution of selected organochlorine compounds and current-use pesticides in snow and lake-sediment samples collected in Rocky Mountain National Park (ROMO) in Colorado and Glacier National Park (GLAC) in Montana during 2002–03. This report also presents estimates of atmospheric deposition rates of selected pesticides to each park and compares the findings with concentrations reported in similar studies in remote mountainous regions. This information can be used to assess if current levels of organic contaminants pose a threat to aquatic organisms and to establish a baseline of information against which changes may be measured in the future. This report includes data for snow samples that were collected at eight sites in ROMO and eight sites in GLAC during spring of 2002 and 2003 and data for surface sediments that were collected at 11 lakes in ROMO and 10 lakes in GLAC during summer months of 2002 and 2003. Snow and sediment samples were analyzed for selected organochlorine compounds and current-use pesticides by three different instrumental techniques.

### Study Area Description

ROMO is located in the Colorado Front Range in north-central Colorado and is characterized by steep, mountainous terrain with elevations ranging from 2,500 m at the eastern park boundary to more than 4,000 m along the Continental Divide (fig. 1). Drainages on the east side of the park form the

headwaters of the Big Thompson River and Saint Vrain Creek, and those on the west side drain into the Upper Colorado River system. The three major ecoregions in ROMO are alpine tundra, subalpine forest, and montane forest. Vegetation in ROMO is dominated by spruce-fir forests between 2,860 and 3,300 m and alpine tundra communities at higher elevations (Baron, 1992). The area is characterized by a continental



**Figure 1.** Rocky Mountain National Park in Colorado showing elevation ranges and major drainages.

climate with long, cold winters and a short growing season (1–3 months). Mean annual precipitation, which varies considerably with elevation, is about 100 cm at 3,150 m. More than one-half of the precipitation occurs as snow that accumulates in a seasonal snowpack between October and April. Winter precipitation is associated with synoptic weather systems with westerly airflow, and summer precipitation is associated with convective air masses originating primarily from the southwest and southeast (Baron and Denning, 1993). Approximately 95 percent of ROMO is designated or recommended as wilderness, and human activities are limited to tourism and recreation. Although the park is adjacent to large areas of undeveloped State and National Forest lands, it is situated less than 40 km to the west of the Front Range urban corridor, which contains the most concentrated population density in the Rocky Mountain region (Dennehy and others, 1993). The park also is situated directly west of large expanses of cropland and pasture on the plains of eastern Colorado. Agricultural pesticide use in this area exceeds 1.3 million kilograms per year and is used primarily to treat corn and hay (Kimbrough and Litke, 1997).

GLAC is located in the northern Rocky Mountains in northwestern Montana and is bounded to the north by the Canadian provinces of Alberta and British Columbia (fig. 2). The North and Middle Forks of the Flathead River border the park on the west and south, and the park is bisected by the Continental Divide. The glaciated landscape, which ranges in elevation from 949 to 3,180 m, is characterized by horn-shaped peaks, broad U-shaped valleys, numerous glacial lakes, and 36 active glaciers. Five large ecoregions are found in GLAC: alpine tundra, subalpine forest, montane forest, aspen parkland, and fescue grassland. Coniferous forests dominate much of the landscape with lodgepole pine, Douglas fir, and western larch growing on drier sites and western hemlock and western red cedar inhabiting wetter sites (White and others, 1998). The climate in GLAC is one of long, cold, snowy winters and relatively short, warm summers. The west side of the park is influenced by Pacific air masses, which result in a milder and moister climate; the east side is dominated by colder Continental air masses. Annual precipitation varies substantially between west-side and east-side locations in the park and ranges from as little as 30 cm at low elevations on the east side to as much as 350 cm at higher elevations on the west side (Finklin, 1986). Most precipitation in winter falls as snow, which accumulates in a seasonal snowpack between November and April. Most of the park is designated wilderness, and human activities are very limited. GLAC is bounded by largely undeveloped National Forest land to the west and south and by the Blackfeet Indian Reservation to the east. Land-use activities in areas adjacent to GLAC include timber harvesting, low-density residential development, road networks, and ranching. Although there is some pesticide use in agricultural areas immediately adjacent to the park, the heaviest use in the region is

in agricultural areas in central Washington and southern Idaho ([http://ca.water.usgs.gov/pnsp/pesticide\\_use\\_maps\\_1997/](http://ca.water.usgs.gov/pnsp/pesticide_use_maps_1997/), accessed December 2005) and to the northeast in Alberta, Canada.

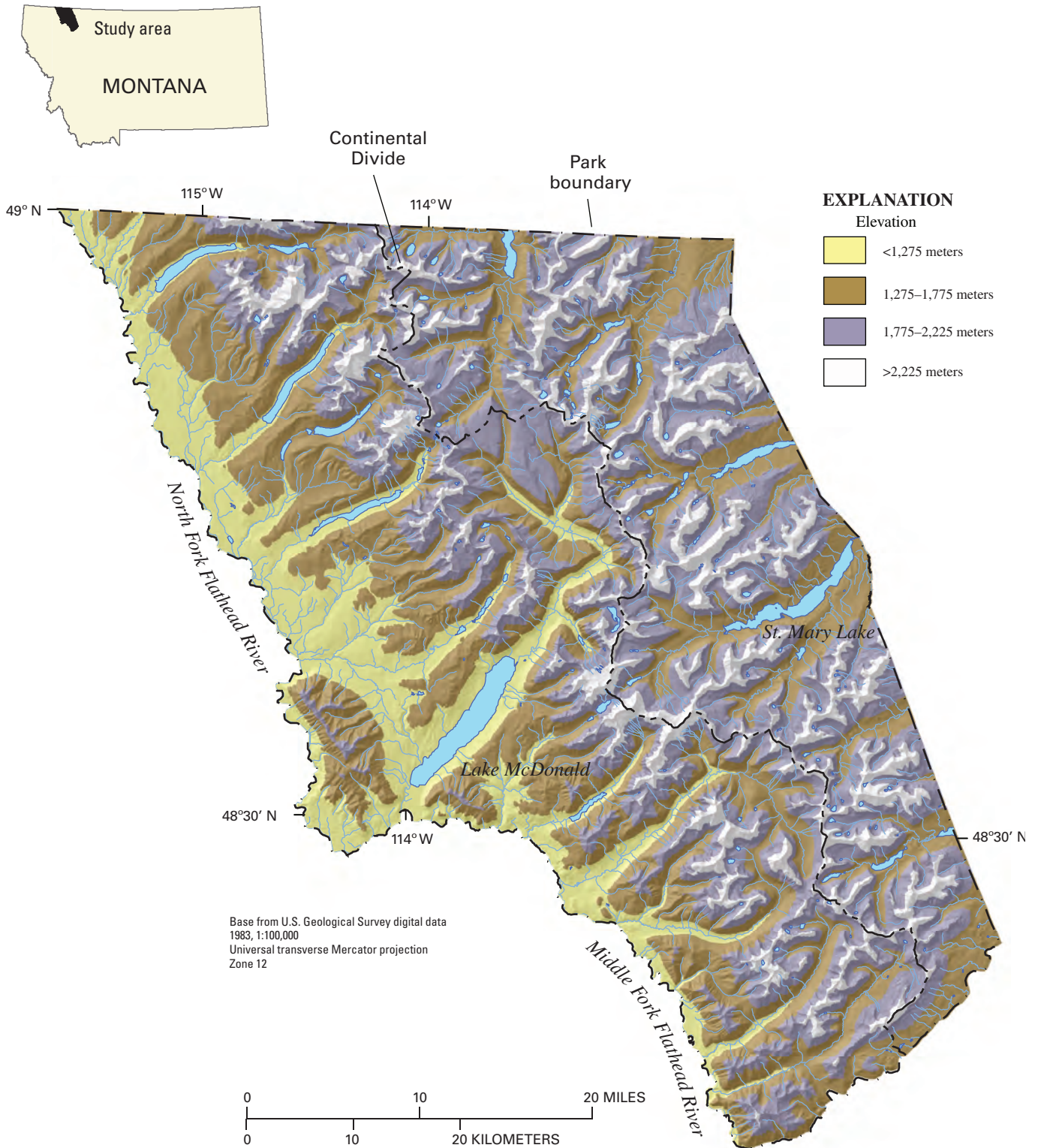
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## Sample Collection and Analytical Methods

### Collection of Snow and Lake-Sediment Samples

Snow samples were collected at eight sites in ROMO and eight sites in GLAC during spring of 2002 and 2003. Snow-sampling sites in each park were established along elevation gradients and on both sides (east and west) of the Continental Divide (table 1, figs. 3–4). Snow samples were collected in late spring at maximum accumulation according to methods developed by Ingersoll and others (2001). Due to the remote location of the sites (fig. 5), all sampling equipment had to be transported on skis into the sampling sites. At each site, a snowpit was excavated and temperature measurements were made along the freshly exposed face to ensure that the snowpack was sampled prior to the onset of spring melt. This timing is important for obtaining a representative sample because some constituents are preferentially eluted from the snowpack during the initial stages of snowmelt (Ingersoll and others, 2001). Snow samples for pesticide analyses were collected from the clean snowpit face into two 20-L PTFE bags using a polycarbonate scoop and shovel. A complete vertical snow column was collected to obtain a sample representative of the entire snowpack. The shovel, scoop, and 20-L PTFE bags were precleaned at a USGS laboratory by washing with laboratory detergent followed by several rinses with tap water, deionized water, methanol, and dichloromethane (DCM). All organic solvents used in this study were pesticide-residue analysis quality. Once filled with snow, the PTFE bags were closed with plastic cable ties and wrapped in aluminum foil to exclude light and then placed in large polypropylene bags



**Figure 2.** Glacier National Park in Montana showing elevation ranges and major drainages.

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**Table 1.** Description of snow-sampling sites in Rocky Mountain National Park and Glacier National Park and analytical methods used.

[No., number in figures 3 and 4; USGS, U.S. Geological Survey; ROMO, Rocky Mountain National Park; GLAC, Glacier National Park; Location, location of sampling site relative to the Continental Divide; Elev., elevation in meters; OCC, organochlorine compounds analyzed by gas chromatography/electron capture detection (GC/ECD); CUP, current-use pesticides analyzed by gas chromatography/electron-impact mass spectrometry (GC/EIMS); OHC, organohalogen compounds analyzed by gas chromatography/electron-capture negative ion mass spectrometry (GC/ECNIMS)]

No.	USGS site number	Site name	Park	Location	Elev.	2002 <sup>1</sup>			2003 <sup>2</sup>	
						OCC	CUP	OHC	CUP	OHC
S1	401848105384200	Bear Lake	ROMO	East	2,934	x	x	--	x	x
S2	401723105395701	Loch Vale Forest	ROMO	East	3,216	x	x	x	x	x
S3	401725105400001	Loch Vale Meadow	ROMO	East	3,215	--	--	--	x	x
S4	401720105403400	Upper Andrews Tarn	ROMO	East	3,402	x	x	x	--	--
S5	402350105505400	Phantom Valley	ROMO	West	2,752	x	x	--	x	x
S6	402443105491600	Lake Irene Meadow	ROMO	West	3,237	--	--	--	x	x
S7	402442105491000	Lake Irene Forest	ROMO	West	3,243	x	--	--	--	--
S8	402530105482000	Forest Canyon Pass	ROMO	West	3,414	x	x	--	--	--
S9	484741113410800	Swiftcurrent Creek	GLAC	East	1,542	x	x	--	--	--
S10	484037113383800	E3	GLAC	East	1,581	x	x	--	--	--
S11	484129113392800	E6	GLAC	East	1,937	x	x	--	--	--
S12	484240113390500	Preston Park	GLAC	East	2,163	x	x	--	--	--
S13	484553113482100	W10	GLAC	West	1,467	x	x	--	--	--
S14	483723113483600	Lower Snyder Lake	GLAC	West	1,585	--	--	--	x	x
S15	484546113473400	W11	GLAC	West	1,753	x	x	--	--	--
S16	484616113461300	Granite Park	GLAC	West	2,006	x	x	--	x	x

<sup>1</sup>2002 samples were prepared by OCC method and initially analyzed by GC/ECD. The same extracts were subsequently analyzed for CUPs by GC/EIMS and OHCs by GC/ECNIMS.

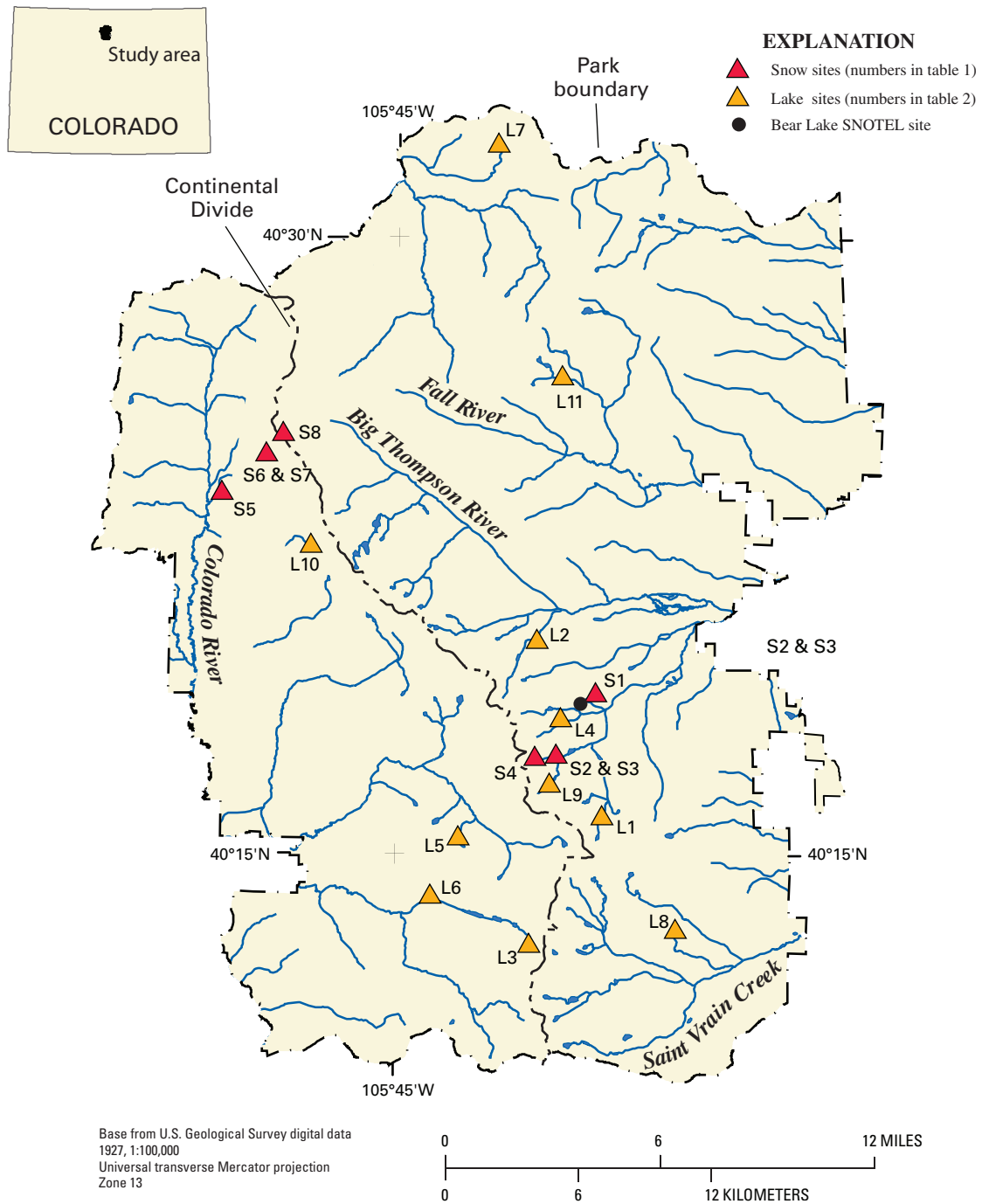
<sup>2</sup>2003 samples were prepared by CUP method and initially analyzed by GC/EIMS. The same extracts were subsequently analyzed for OHCs by GC/ECNIMS.

to prevent puncture of the PTFE bags. Snow samples were transported on dry ice to the laboratory freezer where they were stored at  $-15^{\circ}\text{C}$  for 2 to 3 months before processing and analysis at the USGS National Water Quality Laboratory (NWQL).

Surface sediments were collected at 11 lakes in ROMO and 10 lakes in GLAC during summer months of 2002 and 2003 (table 2, figs. 3–4). Lakes that supported fish populations were selected from each side of the Continental Divide. Cores were collected from a small inflatable raft anchored near the deepest point in each lake by using a gravity benthos corer (fig. 6C). Due to the remote location of the lakes, all sampling equipment had to be backpacked into the sampling sites. The surface sediment (top 3 cm) of each core was extruded from the core tube and transferred into a baked glass jar using a precleaned metal spatula. Based on  $^{210}\text{Pb}$  dating of several sediment cores from each park, the top 3 cm of sediment generally represented lake sediments that were deposited over the past 10–15 years (M.A. Mast, U.S. Geological Survey, unpub. data, 2004). Due to the small diameter of the corer (6 cm), surface sediment from three to five cores had to be combined into one jar to acquire sufficient sample mass for the pesticide analyses. The samples were transported on ice to the laboratory where they were stored frozen ( $-5^{\circ}\text{C}$ ) until analysis at the NWQL.

### Analytical Methods

This study initially was designed to determine organochlorine compounds (OCC) in snow and sediment from the two parks. In 2002, all samples were extracted and analyzed for selected organochlorine pesticides and PCB congeners by gas chromatography with electron-capture detection (GC/ECD); however, none of the OCCs were detected in the snow samples and only a few compounds were detected in the sediment samples. Based on the presence of several current-use pesticides in previously collected snow and rain samples from ROMO (Mast and others, 2001; Mast and others, 2003), the method used for the 2003 snow samples was modified for the extraction and analysis of current-use pesticides (CUP) by gas chromatography with electron-impact mass spectrometry (GC/EIMS). The 2003 sediment samples were extracted and analyzed by both the OCC and CUP methods. Several of the snow and sediment extracts prepared by these two methods also were reanalyzed by gas chromatography with electron-capture negative ion mass spectrometry (GC/ECNIMS). This third instrumental analysis was used to verify detected concentrations in the initial analysis and to investigate the presence of additional organohalogen compounds (OHC). Methods used to prepare and analyze the snow and sediment samples are listed in tables 1 and 2 and analytes determined by each instrumental technique are listed in table 3.



**Figure 3.** Location of snow and lake sampling sites in Rocky Mountain National Park, Colorado.

### Snow

Snow samples were melted in the sealed PTFE bags (two bags per sample) over a 24-hour period at the NWQL, which typically yielded 10 to 15 L of snowmelt. In 2002, 25 ng of organochlorine surrogate  $\alpha$ -HCH-*d6*, isodrin, and PCB 207 and 50 ng of organophosphorus surrogate isofenphos were added to each of the two bags to monitor recoveries from the sample preparation process. Pesticides in the snowmelt were extracted by adding 200 mL of DCM directly to the sample

in the PTFE bag. The melted snow samples were not filtered, so both dissolved and particulate phases were extracted by the solvent, including organic debris (pine needles and immature cones) present in some samples. The DCM was mixed with the sample by using a shaker table, then the extracted water was pumped from the bag to a waste container and the DCM was pumped into a separatory funnel. An additional 50 mL of DCM was used to rinse each PTFE bag and added to the separatory funnel. The combined DCM extracts and bag rinses were drained from the separatory funnel into a baked 1-L glass

8 Organochlorine Compounds and Current-Use Pesticides in Snow and Lake Sediment, 2002–03

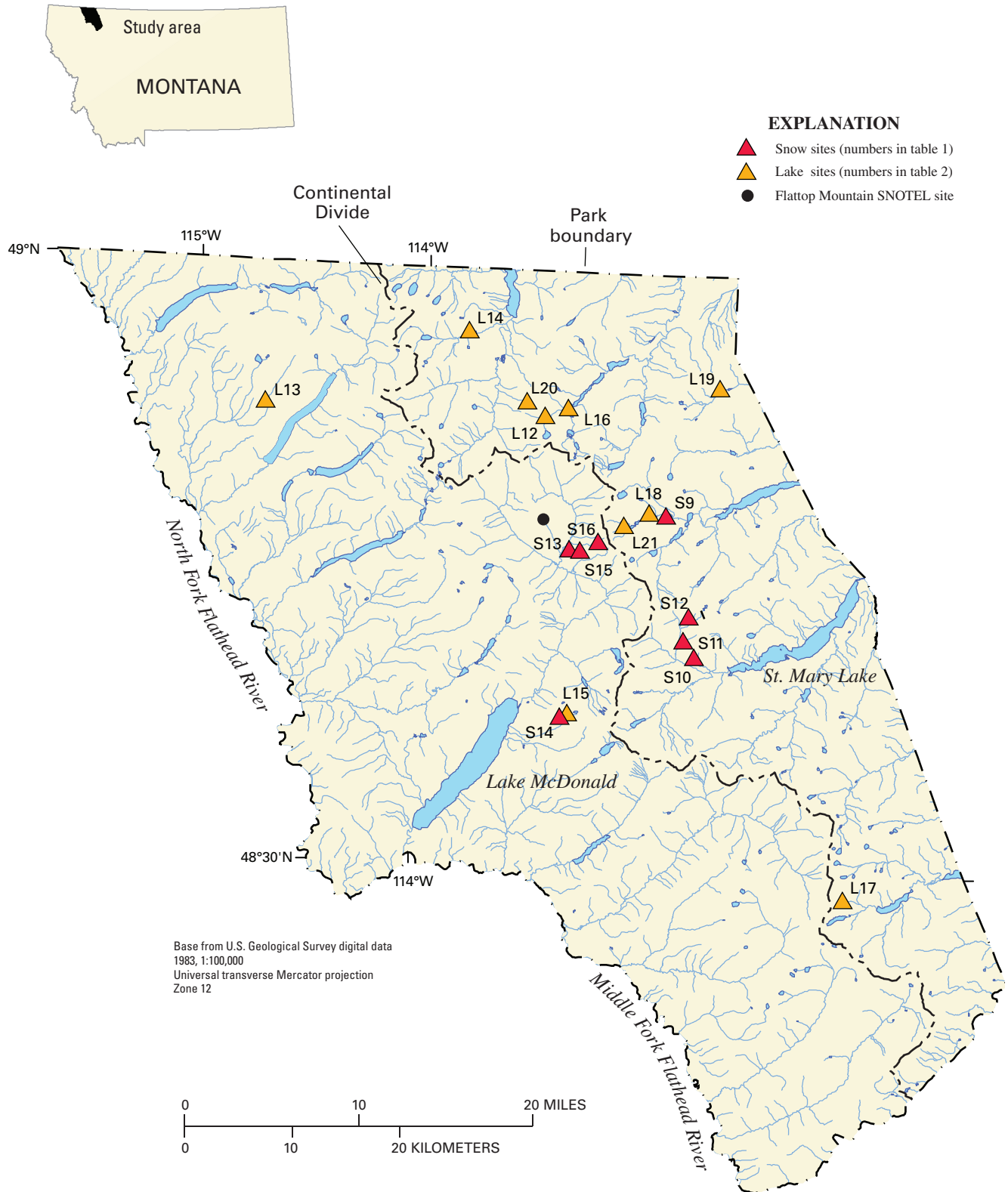


Figure 4. Locations of snow and lake sampling sites in Glacier National Park, Montana.



**Figure 5.** (A) Transport of snow-sampling equipment and samples, (B) preparation of snowpits for sampling, and (C) collection of a sample from the snowpit face.

bottle and dried with sodium sulfate. The extract was reduced in volume and exchanged to hexane using Kuderna-Danish distillation and nitrogen gas evaporation to 1 mL. The extract was cleaned and fractionated using an alumina/silica column according to the method of Noriega and others (2004). The fractions were reduced in volume by micro-Kuderna-Danish distillation and nitrogen gas evaporation to 0.5 mL and transferred to a gas chromatography (GC) vial. Each fraction was

analyzed for 16 organochlorine pesticides and degradates and 27 PCB congeners by dual-capillary-column GC/ECD according to the method of Noriega and others (2004). This extraction procedure and instrumental analysis for organochlorine compounds is referred to as the “OCC” method in this report. No compounds were detected by the OCC method in any of the 2002 snow samples above the reporting levels listed in table 3 and will not be discussed further in this report.



**Table 2.** Description of lake-sediment sampling sites in Rocky Mountain National Park and Glacier National Park and analytical methods used.

[No., number in figures 3 and 4; USGS, U.S. Geological Survey; ROMO, Rocky Mountain National Park; GLAC, Glacier National Park; Location, location of sampling site relative to the Continental Divide; Elev., elevation in meters; OCC, organochlorine compounds analyzed by gas chromatography/electron capture detection (GC/ECD); CUP, current-use pesticides analyzed by gas chromatography/electron-impact mass spectrometry (GC/EIMS); OHC, organohalogen compounds analyzed by gas chromatography/electron-capture negative ion mass spectrometry (GC/ECNIMS)]

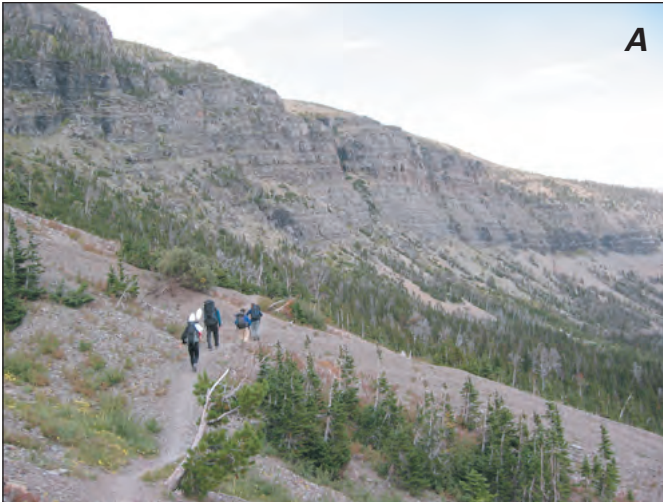
No.	USGS site number	Site name	Park	Location	Elev.	2002		2003	
						OCC	OCC	CUP	OHC <sup>1</sup>
L1	401555105382700	Black Lake	ROMO	East	3,237	--	x	x	x
L2	402011105403801	Fern Lake	ROMO	East	2,903	x	--	--	--
L3	401247105404400	Fifth Lake	ROMO	West	3,280	x	--	--	--
L4	401817105394500	Lake Haiyaha	ROMO	East	3,115	--	x	x	x
L5	401523105430000	Lake Nanita	ROMO	West	3,267	x	--	--	--
L6	401324105435400	Lone Pine Lake	ROMO	West	3,078	x	--	--	--
L7	403215105415200	Mirror Lake	ROMO	East	3,359	x	--	--	--
L8	401308105360500	Sandbeach Lake	ROMO	East	3,134	x	--	--	--
L9	401643105400100	Sky Pond	ROMO	East	3,316	x	--	--	--
L10	402227105474501	Timber Lake	ROMO	West	3,371	x	--	--	--
L11	402636105394100	Ypsilon Lake	ROMO	East	3,200	--	x	x	x
L12	485230113503300	Atsina Lake	GLAC	East	1,757	--	x	x	x
L13	485244114115400	Akokala Lake	GLAC	West	1,463	x	--	--	--
L14	485639113563600	Lake Janet	GLAC	East	1,512	--	x	x	x
L15	483736113481100	Lower Snyder Lake	GLAC	West	1,585	x	--	--	--
L16	485254113485000	Mokowanis Lake	GLAC	East	1,524	--	x	x	x
L17	482844113265000	Noname Lake	GLAC	East	1,817	x	--	--	--
L18	484746113422300	Redrock Lake	GLAC	East	1,536	x	--	--	--
L19	485407113372500	Slide Lake	GLAC	East	1,838	--	x	x	x
L20	485309113515800	Stoney Indian Lake	GLAC	East	1,926	--	x	x	x
L21	484709113441900	Upper Bullhead Lake	GLAC	East	1,585	x	--	--	--

<sup>1</sup>Samples were prepared by CUP sediment method and initially analyzed by GC/EIMS. The same extracts were subsequently analyzed for OHCs by GC/ECNIMS.

In 2003, the method used to process snow samples was targeted toward analysis of current-use pesticides and is referred to as the “CUP” method in this report. The melted snow sample in each bag was fortified with 50 ng of  $\alpha$ -HCH-*d6* and diazinon-*d10* surrogates and then poured through a coarse filter (to remove pine needles and other debris greater than 1 mm) into a 6-L separatory funnel. The samples were shake extracted using 200-mL aliquots of DCM per 5 L of meltwater plus 50 mL of DCM used to rinse the bag. The DCM extracts and bag rinses for each sample were combined in a baked 1-L glass bottle and dried with sodium sulfate. The extract was reduced in volume and exchanged to ethyl acetate using Kuderna-Danish distillation and nitrogen gas evaporation to 1 mL. The extract was passed through a graphitized carbon solid-phase extraction column (CarboPrep 90), and the analytes were eluted with 13 mL of a solution of 50 percent DCM in ethyl acetate. A procedural internal standard solution of three perdeuterated polycyclic aromatic hydrocarbons (PAH) was added to the extract before final solvent reduction and exchange to toluene using nitrogen

gas evaporation. The extract was transferred to a GC vial with toluene rinse to 0.25-mL final volume and analyzed for 62 current-use pesticides by GC/EIMS operated in the selected-ion monitoring mode using conditions described in Zaugg and others (1995), Sandstrom and others (2001), and Madsen and others (2003). The 2002 snow extracts prepared by the OCC method also were analyzed for CUPs by GC/EIMS; however, only 18 of the 62 current-use pesticides were recovered from the alumina/silica cleanup procedure and could be quantified.

The 2002 snow extracts (prepared by the OCC method) and 2003 snow extracts (prepared by the CUP method) also were analyzed for a variety of organohalogen compounds by gas chromatography with electron-capture negative ion mass spectrometry (GC/ECNIMS), referred to as the “OHC” instrumental analysis in this report. The compounds determined by the OHC analysis include selected organochlorine and current-use pesticides (several of which also were analyzed by the OCC and CUP methods) and selected PCB congeners and PBDE flame retardants (table 3).



**Figure 6.** (A) Transport of sediment sampling gear to a lake in Glacier National Park, (B) crew working from an inflatable boat, and (C) collection of surface sediment from lake core.

**Table 3.** Pesticides and other organic compounds analyzed in snow and sediment samples collected during this study.

[D, degradate; E, all concentrations for this compounds reported as estimated; F, fungicide; H, herbicide; I, insecticide; M, manufacturing or byproduct; R, flame retardant; TEC, threshold effect concentration; PEC, probable effect concentration; --, not analyzed or not available; µg/L, microgram per liter; µg/kg, microgram per kilogram; ng/L, nanogram per liter; PCB, polychlorinated biphenyls; PBDE, polybrominated diphenyl ethers]

Compound	Chemical Abstract Service registry number	Type of compound	Aquatic-life criterion, Water chronic <sup>1</sup> (µg/L)	Aquatic-life criterion, Sediment TEC (PEC) <sup>2</sup> (µg/kg)	Determined for snow samples	Determined for sediment samples	Reporting limit for OCC snow method <sup>3</sup> (ng/L)
Organochlorine compounds (OCC) analyzed by gas chromatography with electron-capture detection (GC/ECD)							
Aldrin	309-00-2	I	--	--	2002	2002-03	1.9
Chlordane, technical	57-74-9	I	--	3.24 (17.6)	--	2002-03	--
<i>cis</i> -Chlordane	5103-71-9	I	--	--	2002	2003	2.4
<i>trans</i> -Chlordane	5103-74-2	I	--	--	2002	2003	2.4
<i>p,p'</i> -DDT	50-29-3	I	--	4.16 (62.9)	2002	2002-03	1.9
<i>p,p'</i> -DDD	72-54-8	D	--	4.88 (28.0)	2002	2002-03	2.4
<i>p,p'</i> -DDE	72-55-9	D	--	3.16 (31.3)	2002	2002-03	1.9
Dieldrin	60-57-1	I	0.056	1.90 (61.8)	2002	2002-03	2.0
Endosulfan I	959-98-8	I	--	--	2002	2002-03	2.1
Endrin	72-20-8	I	--	2.22 (207)	2002	2002-03	1.9
γ-HCH (Lindane)	58-89-9	I	0.01	2.37 (4.99)	2002	2002-03	2.0
Heptachlor	76-44-8	I	--	--	2002	2002-03	1.5
Heptachlor epoxide	1024-57-3	D	--	2.47 (16.0)	2002	2002-03	2.6
<i>p,p'</i> -Methoxychlor	72-43-5	I	--	--	2002	2002-03	2.8
Mirex	2385-85-5	I	--	--	2002	2002-03	2.4
<i>trans</i> -Nonachlor	39765-80-5	I	--	--	2002	2003	2.4
PCBs as Aroclor 1242	53469-21-9	M	--	--	--	2002-03	--
PCBs as Aroclor 1254	11097-69-1	M	--	--	--	2002-03	--
PCBs as Aroclor 1260	11097-69-1	M	--	--	--	2002-03	--
Toxaphene	8001-35-2	I	--	--	2002	2002-03	1,000
Current-use pesticides (CUP) analyzed by gas chromatography with electron-impact mass spectrometry (GC/EIMS)							
Acetochlor	34256-82-1	H	--	--	2002-03	2003	
Alachlor	15972-60-8	H	--	--	2002-03	2003	
2-Chloro-2,6-diethylacetamide	6967-29-9	D	--	--	2003	2003	
2,6-Diethylamine (E)	579-66-8	D	--	--	2002-03	2003	
Atrazine	1912-24-9	H	1.8	--	2003	2003	
2-Chloro-4-isopropylamino-6-amino-s-triazine	6190-65-4	D	--	--	2003	2003	
Azinphos-methyl (E)	86-50-0	I	0.01	--	2003	2003	
Azinphos-methyl-oxon (E)	961-22-8	D	--	--	2003	2003	
Benfluralin	1861-40-1	H	--	--	2002-03	2003	
Carbaryl (E)	63-25-2	I	0.2	--	2003	2003	
1-Naphthol (E)	90-15-3	D	--	--	2003	2003	
4-Chloro-2-methylphenol (E)	1570-64-5	D	--	--	2003	2003	

**Table 3.** Pesticides and other organic compounds analyzed in snow and sediment samples collected during this study.—Continued

[D, degradate; E, all concentrations for this compounds reported as estimated; F, fungicide; H, herbicide; I, insecticide; M, manufacturing or byproduct; R, flame retardant; TEC, threshold effect concentration; PEC, probable effect concentration; --, not analyzed or not available; µg/L, microgram per liter; µg/kg, microgram per kilogram; ng/L, nanogram per liter; µg/L, microgram per liter; µg/kg, microgram per kilogram; ng/L, nanogram per liter; PCB, polychlorinated biphenyls; PBDE, polybrominated diphenyl ethers]

Compound	Chemical Abstract Service registry number	Type of compound	Aquatic-life criterion, Water chronic <sup>1</sup> (µg/L)	Aquatic-life criterion, Sediment TEC (PEC) <sup>2</sup> (µg/kg)	Determined for snow samples	Determined for sediment samples	Reporting limit for OCC snow method <sup>3</sup> (ng/L)
Current-use pesticides (CUP) analyzed by gas chromatography with electron-impact mass spectrometry (GC/EIMS)—Continued							
Chlorpyrifos	2921-88-2	I	0.041	--	2002-03	2003	
Chlorpyrifos, oxygen analog (E)	5598-15-2	D	--	--	2003	2003	
Cyfluthrin (E)	68359-37-5	I	--	--	2003	2003	
Cypermethrin (E)	52315-07-8	I	--	--	2003	2003	
Dacthal	1861-32-1	H	--	--	2002-03	2003	
Diazinon	333-41-5	I	0.08	--	2002-03	2003	
Diazinon, oxygen analog (E)	962-58-3	D	--	--	2002-03	2003	
3,4-Dichloroaniline (E)	95-76-1	D	--	--	2003	2003	
Dichlorvos (E)	62-73-7	I	--	--	2003	2003	
Dicrotophos (E)	141-66-2	I	--	--	2003	2003	
Dieldrin	60-57-1	I	0.056	1.90 (61.8)	2002-03	2003	
Dimethoate	60-51-5	I	--	--	2003	2003	
Ethion	563-12-2	I	--	--	2002-03	2003	
Ethion monoxon	17356-42-2	D	--	--	2003	2003	
Fenamiphos (E)	22224-92-6	I	--	--	2003	2003	
Fenamiphos sulfone (E)	31972-44-8	D	--	--	2003	2003	
Fenamiphos sulfoxide (E)	31972-43-7	D	--	--	2003	2003	
Fipronil (E)	120068-37-3	I	--	--	2003	2003	
Fipronil sulfide (E)	120067-83-6	D	--	--	2003	2003	
Fipronil sulfone	120068-36-2	D	--	--	2003	2003	
Fipronil, desulfanyl		D	--	--	2003	2003	
Fipronil amide, desulfanyl (E)		D	--	--	2003	2003	
Fonofos	944-22-9	I	--	--	2002-03	2003	
Hexazinone	51235-04-2	H	--	--	2003	2003	
Iprodione (E)	36734-19-7	F	--	--	2003	2003	
Isofenphos	25311-71-1	I	--	--	2002-03	2003	
Malathion	121-75-5	I	0.1	--	2003	2003	
Malathion, oxygen analog (E)	1634-78-2	D	--	--	2003	2003	
Metaxyl	57837-19-1	F	--	--	2003	2003	
Methodathion	950-37-8	I	--	--	2003	2003	
Metolachlor	51218-45-2	H	7.8	--	2003	2003	
2-Ethyl-6-methylamine (E)	24549-06-2	D	--	--	2002-03	2003	
Metribuzin	21087-64-9	H	1.0	--	2003	2003	
Myclobutanil (E)	88671-89-0	F	--	--	2003	2003	

**Table 3.** Pesticides and other organic compounds analyzed in snow and sediment samples collected during this study.—Continued

[D, degradate; E, all concentrations for this compounds reported as estimated; F, fungicide; H, herbicide; I, insecticide; M, manufacturing or byproduct; R, flame retardant; TEC, threshold effect concentration; PEC, probable effect concentration; --, not analyzed or not available; µg/L, microgram per liter; µg/kg, microgram per kilogram; ng/L, nanogram per liter; PCB, polychlorinated biphenyls; PBDE, polybrominated diphenyl ethers]

Compound	Chemical Abstract Service registry number	Type of compound	Aquatic-life criterion, Water chronic <sup>1</sup> (µg/L)	Aquatic-life criterion, Sediment TEC (PEC) <sup>2</sup> (µg/kg)	Determined for snow samples	Determined for sediment samples	Reporting limit for OCC snow method <sup>3</sup> (ng/L)
Current-use pesticides (CUP) analyzed by gas chromatography with electron-impact mass spectrometry (GC/EIMS)—Continued							
Parathion-methyl	298-00-0	I	0.013	--	2003	2003	2003
Parathion-methyl. Oxygen analog (E)	950-35-6	D	--	--	2003	2003	2003
Pendimethalin	40487-42-1	H	--	--	2002	2003	2003
<i>cis</i> -Permethrin	54774-45-7	I	--	--	2002	2003	2003
Phorate (E)	298-02-2	I	--	--	2003	2003	2003
Phorate, oxygen analog (E)	2600-69-3	D	--	--	2003	2003	2003
Prometon (E)	1610-18-0	H	--	--	2003	2003	2003
Prometryn	7287-19-6	H	--	--	2003	2003	2003
Propylzamide	23950-58-5	H	--	--	2002-03	2003	2003
Simazine	122-34-9	H	10	--	2003	2003	2003
Tebuthiuron (E)	34014-18-1	H	--	--	2003	2003	2003
Terbufos	13071-79-9	I	--	--	2003	2003	2003
Terbufos-oxygen analog sulfone (E)	56070-15-6	D	--	--	2003	2003	2003
Terbutylazine	5915-41-3	H	--	--	2003	2003	2003
Trifluralin	1582-09-8	H	0.2	--	2002-03	2003	2003
Organohalogen compounds (OHC) analyzed by gas chromatography with electron-capture negative ion mass spectrometry (GC/ECNIMS)							
Aldrin	309-00-2	I	--	--	2002-03	2003	2003
Benfluralin	1861-40-1	H	--	--	2002-03	2003	2003
<i>cis</i> -Chlordane	5103-71-9	I	--	--	2002-03	2003	2003
<i>trans</i> -Chlordane	5103-74-2	I	--	--	2002-03	2003	2003
Oxychlordane	27304-13-8	D	--	--	2002-03	2003	2003
Chlorothaloniil (E)		F	0.18	--	2003	--	--
Dacthal (DCPA)	1861-32-1	H	--	--	2002-03	2003	2003
<i>o,p'</i> -DDD	53-19-0	D	--	--	2002-03	2003	2003
<i>o,p'</i> -DDE	3424-82-6	D	--	--	2002-03	2003	2003
<i>p,p'</i> -DDE	72-55-9	D	--	3.16 (31.3)	2002-03	2003	2003
Dieldrin	60-57-1	I	0.056	1.90 (61.8)	2002-03	2003	2003
Endosulfan I	959-98-8	I	--	--	2002-03	2003	2003
Endosulfan II	33213-65-9	I	--	--	2002-03	2003	2003
Endosulfan sulfate	1031-07-8	D	--	--	2003	2003	2003

**Table 3.** Pesticides and other organic compounds analyzed in snow and sediment samples collected during this study.—Continued

[D, degradate; E, all concentrations for this compounds reported as estimated; F, fungicide; H, herbicide; I, insecticide; M, manufacturing or byproduct; R, flame retardant; TEC, threshold effect concentration; PEC, probable effect concentration; --, not analyzed or not available; µg/L, microgram per liter; µg/kg, microgram per kilogram; ng/L, nanogram per liter; µg/L, microgram per liter; PCB, polychlorinated biphenyls; PBDE, polybrominated diphenyl ethers]

Compound	Chemical Abstract Service registry number	Type of compound	Aquatic-life criterion, Water chronic <sup>1</sup> (µg/L)	Aquatic-life criterion, Sediment TEC (PEC) <sup>2</sup> (µg/kg)	Determined for snow samples	Determined for sediment samples	Reporting limit for OCC snow method <sup>3</sup> (ng/L)
Organohalogen compounds (OHC) analyzed by gas chromatography with electron-capture negative ion mass spectrometry (GC/ECNIMS)—Continued							
Endrin	72-20-8	I	--	2.22 (207)	2002-03	2003	
Endrin aldehyde (E)	7421-93-4	D	--	--	2003	2003	
Endrin ketone (E)	53494-70-5	D	--	--	2003	2003	
Fipronil (E)	120068-37-3	I	--	--	2003	2003	
Fipronil sulfide	120067-83-6	D	--	--	2003	2003	
Fipronil sulfone	120068-36-2	D	--	--	2003	2003	
Fipronil, desulfinyl	--	D	--	--	2003	2003	
Fipronil amide, desulfinyl (E)	--	D	--	--	2003	2003	
Heptachlor	76-44-8	I	--	--	2002-03	2003	
Heptachlor epoxide	1024-57-3	D	--	2.47 (16.0)	2002-03	2003	
Hexachlorobenzene (HCB)	118-74-1	F, M	--	--	2002	2003	
α-HCH	319-84-6	I	--	--	2002-03	2003	
β-HCH	319-85-7	I	--	--	--	2003	
δ-HCH	319-86-8	I	--	--	2002-03	2003	
γ-HCH (Lindane)	58-89-9	I	0.01	2.37 (4.99)	2002-03	2003	
Isodrin	465-73-6	S, I	--	--	2002-03	2003	
Mirex	2385-85-5	I	--	--	2002-03	2003	
cis-Nonachlor	5103-73-1	I	--	--	2002-03	2003	
trans-Nonachlor	39765-80-5	I	--	--	2002-03	2003	
Octachlorostyrene (E)	29082-74-4	M	--	--	2003	2003	
Pentachloroanisole (PCA)	1825-21-4	D	--	--	2002-03	2003	
Trifluralin	1582-09-8	H	0.02	--	2002-03	2003	
<i>PCB congeners</i>							
PCB 70	32598-11-1	M	--	--	2002-03	2003	
PCB 101	37680-73-2	M	--	--	2002-03	2003	
PCB 110	38380-03-9	M	--	--	2002-03	2003	
PCB 118	31508-00-6	M	--	--	2002-03	2003	
PCB 138	35065-28-2	M	--	--	2002-03	2003	
PCB 146	51908-16-8	M	--	--	2002-03	2003	
PCB 149	38380-04-0	M	--	--	2002-03	2003	

**Table 3.** Pesticides and other organic compounds analyzed in snow and sediment samples collected during this study.—Continued

[D, degradate; E, all concentrations for this compounds reported as estimated; F, fungicide; H, herbicide; I, insecticide; M, manufacturing or byproduct; R, flame retardant; TEC, threshold effect concentration; PEC, probable effect concentration; --, not analyzed or not available; µg/L, microgram per liter; µg/kg, microgram per kilogram; ng/L, nanogram per liter; PCB, polychlorinated biphenyls; PBDE, polybrominated diphenyl ethers]

Compound	Chemical Abstract Service registry number	Type of compound	Aquatic-life criterion, Water chronic <sup>1</sup> (µg/L)	Aquatic-life criterion, Sediment TEC (PEC) <sup>2</sup> (µg/kg)	Determined for snow samples	Determined for sediment samples	Reporting limit for OCC snow method <sup>3</sup> (ng/L)
Organohalogen compounds (OHC) analyzed by gas chromatography with electron-capture negative ion mass spectrometry (GC/ECNIMS)—Continued							
<i>PCB congeners</i> —Continued							
PCB 151	52663-63-5	M	--	--	2002-03	2003	
PCB 170	35065-30-6	M	--	--	2002-03	2003	
PCB 174	38411-25-5	M	--	--	2002-03	2003	
PCB 177	52663-70-4	M	--	--	2002-03	2003	
PCB 180	35065-29-3	M	--	--	2002-03	2003	
PCB 183	52663-69-1	M	--	--	2002-03	2003	
PCB 187	52663-68-0	M	--	--	2002-03	2003	
PCB 194	35694-08-7	M	--	--	2002-03	2003	
PCB 206	40186-72-9	M	--	--	2002-03	2003	
<i>PBDE congeners</i>							
PBDE 47	66115-57-9	R	--	--	2002-03	2003	
PBDE 99	81397-99-1	R	--	--	2002-03	2003	
PBDE 100	97038-97-6	R	--	--	2002-03	2003	
PBDE 153	59080-40-9	R	--	--	2002-03	2003	
PBDE 154	36402-15-0	R	--	--	2002-03	2003	

<sup>1</sup>Standards obtained at <http://ca.water.usgs.gov/pnsp/ansrat/index.html#hdr3> (accessed December 2005).<sup>2</sup>Consensus-based standards from MacDonald and others (2000).<sup>3</sup>Reporting levels for other methods/matrices provided in data tables.

Before OHC analysis, the 2002 OCC extracts were reduced in volume from 0.5 mL to about 0.15 mL using nitrogen evaporation. Only two of the 2002 snow samples were actually analyzed for OHCs because most of the samples were lost during this solvent-reduction step. All seven of the 2003 snow extracts were successfully analyzed by the OHC instrumental technique. For the analysis, 10 ng of dibromooctafluorobiphenyl was added to the extracts as an internal injection standard. Analytes were separated on a 30-m by 0.25-mm-internal-diameter capillary column (Restek Rtx-5MS) with 0.25- $\mu$ m film thickness using the following oven temperature program: 80 degrees Celsius ( $^{\circ}$ C) for 5 min, 10 $^{\circ}$ C/min to 125 $^{\circ}$ C, 1.5 $^{\circ}$ C/min to 200 $^{\circ}$ C, and 8 $^{\circ}$ C/min to 325 $^{\circ}$ C (hold for 20 min). Extract introduction to the gas chromatograph was by splitless injection at 285 $^{\circ}$ C at a helium carrier gas flow rate of about 2 mL/min. Mass spectrometer source and analyzer temperatures were 160 $^{\circ}$ C and 140 $^{\circ}$ C, respectively. Mass spectrometer scan range was 50–600 daltons. Methane was used as the modifying gas at a source ion gage pressure of 0.027 pascal.

## Lake Sediment

Lake sediments were prepared and analyzed for OCCs, including selected PCB congeners, by dual-capillary-column GC/ECD according to the method of Noriega and others (2004). Because PCB congeners were not detected in any of the 2002 samples, PCBs were not analyzed for in the 2003 sediments. Separate aliquots of the lake sediments collected in 2003 also were prepared and analyzed for CUPs by the method described by Foreman and others (2005). Samples were centrifuged to remove excess water, homogenized, and analyzed for dry weight on a 1.5 to 3 g aliquot. A 5 to 44 g aliquot was mixed with Hydromatrix to disperse the sediment matrix and bind residual sediment moisture and was extracted with 25-percent acetone in DCM at 100 $^{\circ}$ C under pressurized conditions (10,342 kPa) to isolate analytes in organic solvent. Resultant extracts were concentrated and cleaned up on a graphitized carbon, solid-phase extraction column as described above for the CUP snow method. The eluent was reduced using micro-Kuderna-Danish distillation and nitrogen gas evaporation to 2.5 mL. The analytes were further isolated from elemental sulfur and some additional unwanted coextractants by gel permeation chromatography on a portion of the extract using a 300-mm-long by 7.5-mm-internal-diameter polystyrene divinylbenzene column (Polymer Laboratories, Ltd., PL gel column containing 5- $\mu$ m-diameter particles with 50-angstrom pores) with ethyl acetate mobile phase at 1-mL/min flow rate. The 9-mL collected gel permeation chromatography fraction was reduced as a hexane/ethyl acetate azeotrope by micro-Kuderna-Danish distillation to 1–2 mL. A procedural internal standard solution of perdeuterated PAHs was added to the extract before final solvent reduction and exchange to toluene using nitrogen gas evaporation.

The extract was transferred to a GC vial with toluene rinse to 0.5-mL final volume and analyzed for CUPs by GC/EIMS and then for OHCs by GC/ECNIMS, as described for the 2003 snow samples.

## Reporting Levels

Analyte concentrations are reported using the convention outlined in Childress and others (1999). The OCC snow and sediment methods use a minimum reporting level (MRL), which is the minimum concentration of a compound that can be reliably reported for an analytical method. No concentrations are reported less than the MRL for the OCC method. Reporting levels are preceded by a “<” symbol in the data tables (tables 4–9, 11–15, and 17–20, presented later in the report). The CUP sediment method used an interim reporting level (Sandstrom and others, 2001) comparable in scope to the laboratory reporting level described in Childress and others (1999). Reporting levels listed for CUPs and OHCs in snow and OHCs in sediment were estimated on the basis of sample volume, analyte recovery, and instrument detection capability for low-concentration calibration standards during the analysis periods. In some cases, reporting levels were raised because of interferences in samples or blank contamination. For all mass spectrometric analyses, concentrations of an analyte less than the reporting level or lowest calibration standard (whichever was higher) are reported as estimated (E) concentrations. In these cases, the presence of the pesticide has been verified, but the concentration is estimated because it falls below the range of the calibration standards. Some compounds (table 3) are always reported as estimated regardless of concentration because of recognized performance issues (Childress and others, 1999; Sandstrom and others, 2001). In the remainder of this report, estimated concentrations were treated as normal detected concentrations.

## Field Quality Control

Field blanks were used to assess potential contamination of a sample from collection and processing procedures. For snow samples, one equipment blank and two field blanks were collected during the study. The equipment blank was processed in the laboratory using the same equipment used to collect snow samples whereas the field blanks were collected at the field site. Field blanks were not collected with any of the sediment samples due to the lack of a representative blank material. Snow-sample blanks were prepared by pouring commercially available pesticide-residue grade water over the sampling scoop and shovel into the PTFE bag. The blank samples were stored in the same freezer with the field samples and melted and processed along with the snow samples. No CUPs (table 4) or OHCs (table 5) were detected in the three snow blanks with the exception of two PCB congeners (PCB 118



and PCB 138), which were detected in the 2003 field blank (table 5). Because these congeners were not detected in the laboratory blanks or in any of the environmental samples, the results indicate that the reagent water used for this sample might have been contaminated. Aside from these two congeners, the blank results indicate the potential for contamination of snow samples from sample-collection and processing procedures was minimal.

Field replicate samples were used to provide information on the precision of concentration values and the consistency in identifying the compounds of interest in the environmental samples. Field replicates for snow were collected at two sites in 2002 and two sites in 2003. Results for CUPs in field replicates are presented in table 4, and results for OHCs are presented in table 5. Concentrations of CUPs in the snow replicates were below the estimated reporting levels for all of the target compounds except for dacthal (table 4). The relative percent difference (RPD) in dacthal concentrations, calculated as the difference in concentration between replicates divided

by the average concentration, shows greater variability in the 2002 replicates (111 RPD for Bear Lake and 140 RPD for W10) compared to the 2003 replicates (70 RPD for Loch Vale and 54 RPD for Lake Irene). One possible explanation for the poor agreement between 2002 replicates is that these extracts were stored for nearly a year before being analyzed for CUPs. Another consideration is that some 2002 snow samples contained small but variable amounts of organic debris (needles and immature cones), which also might have contributed to concentration differences (Reischl and others, 1987; Horstmann and McLaughlin, 1998). Larger (>1-mm diameter) plant debris was removed from 2003 snow samples prior to extraction to minimize their potential contribution. Five OHCs were detected in both replicate pairs indicating there was good reliability in identifying the target OHCs (table 5). Although dieldrin and *trans*-nonachlor were detected in the Lake Irene environmental sample but not the replicate sample, the concentrations were reported as estimated and were below the reporting level for both compounds. Relative

**Table 4.** Concentrations of current-use pesticides analyzed by gas chromatography/electron-impact mass spectrometry in field blanks and replicate snow samples collected in 2002–03.

[Equip, equipment; Environ, environmental sample; Repl, replicate sample; <, less than; --, not determined; ns, not in spike or surrogate; %, percent; concentrations in nanograms per liter; shaded cells denote detectable concentrations; OCC, organochlorine compounds by gas chromatography/electron-capture detection (GC/ECD); CUP, current-use pesticides by gas chromatography/electron-impact mass spectrometry (GC/EIMS)]

Compound	2002 <sup>1</sup> Blank		2003 Blank	2002 <sup>1</sup> Bear Lake		2002 <sup>1</sup> W10		2003 Loch Vale Forest		2003 Lake Irene Meadow	
	Equip	Field	Field	Environ	Repl	Environ	Repl	Environ	Repl	Environ	Repl
Acetochlor	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60
Alachlor	<13	<13	<8.0	<13	<13	<13	<13	<8.0	<8.0	<8.0	<8.0
Atrazine	--	--	<1.5	--	--	--	--	<1.5	<1.5	<1.5	<1.5
Azinphos-methyl	--	--	<5.0	--	--	--	--	<8.7	<5.0	<5.0	<5.0
Azinphos-methyl-oxygen analog	--	--	<11	--	--	--	--	<11	<11	<11	<11
Benfluralin	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Carbaryl	--	--	<4.1	--	--	--	--	<4.1	<4.1	<4.1	<4.1
2-Chloro-2,6-diethylacetanilide	--	--	<0.50	--	--	--	--	<0.50	<0.50	<0.50	<0.50
2-Chloro-4-isopropylamino-6-amino-s-triazine	--	--	<0.60	--	--	--	--	<0.60	<0.60	<0.60	<0.60
4-Chloro-2-methylphenol	--	--	<0.56	--	--	--	--	<0.56	<0.56	<0.56	<0.56
Chlorpyrifos	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50
Chlorpyrifos, oxygen analog	--	--	<5.6	--	--	--	--	<5.6	<5.6	<5.6	<5.6
Cyfluthrin	--	--	<2.7	--	--	--	--	<2.7	<2.7	<2.7	<2.7
Cypermethrin	--	--	<0.86	--	--	--	--	<0.86	<0.86	<0.86	<0.86
Dacthal	<0.30	<0.30	<0.80	2.20	0.63	0.27	1.53	0.48	1.00	1.08	1.88
Diazinon	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50
Diazinon, oxygen analog	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60
3,4-Dichloroaniline	--	--	<0.45	--	--	--	--	<0.45	<0.45	<0.45	<0.45
Dichlorvos	--	<1.2	<1.2	--	--	--	--	<1.2	<1.2	<1.2	<1.2
Dicrotophos	--	<8.4	<8.4	--	--	--	--	<8.4	<8.4	<8.4	<8.4
Dieldrin	<0.90	<0.90	<0.90	<0.90	<0.90	<0.90	<0.90	<0.90	<0.90	<0.90	<0.90
2,6-Diethylaniline	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60
Dimethoate	--	--	<0.61	--	--	--	--	<0.61	<0.61	<0.61	<0.61

**Table 4.** Concentrations of current-use pesticides analyzed by gas chromatography/electron-impact mass spectrometry in field blanks and replicate snow samples collected in 2002–03.—Continued

[Equip, equipment; Environ, environmental sample; Repl, replicate sample; <, less than; --, not determined; ns, not in spike or surrogate; %, percent; concentrations in nanograms per liter; shaded cells denote detectable concentrations; OCC, organochlorine compounds by gas chromatography/electron-capture detection (GC/ECD); CUP, current-use pesticides by gas chromatography/electron-impact mass spectrometry (GC/EIMS)]

Compound	2002 <sup>1</sup> Blank		2003 Blank	2002 <sup>1</sup> Bear Lake		2002 <sup>1</sup> W10		2003 Loch Vale Forest		2003 Lake Irene Meadow	
	Equip	Field	Field	Environ	Repl	Environ	Repl	Environ	Repl	Environ	Repl
Ethion	<0.40	<0.40	<0.40	<0.40	<0.40	<0.40	<0.40	<0.40	<0.40	<0.40	<0.40
Ethion monoxon	--	--	<0.20	--	--	--	--	<0.20	<0.20	<0.20	<0.20
2-Ethyl-6-methylaniline	<0.45	<0.45	<0.45	<0.45	<0.45	<0.45	<0.45	<0.45	<0.45	<0.45	<0.45
Fenamiphos	--	--	<2.9	--	--	--	--	<2.9	<2.9	<2.9	<2.9
Fenamiphos sulfone	--	--	<4.9	--	--	--	--	<4.9	<4.9	<4.9	<4.9
Fenamiphos sulfoxide	--	--	<3.9	--	--	--	--	<3.9	<3.9	<3.9	<3.9
Fipronil	--	--	<1.6	--	--	--	--	<1.6	<1.6	<1.6	<1.6
Fipronil sulfide	--	--	<1.3	--	--	--	--	<1.3	<1.3	<1.3	<1.3
Fipronil sulfone	--	--	<2.4	--	--	--	--	<2.4	<2.4	<2.4	<2.4
Fipronil, desulfinyl	--	--	<1.2	--	--	--	--	<1.2	<1.2	<1.2	<1.2
Fipronil amide, desulfinyl	--	--	<2.9	--	--	--	--	<2.9	<2.9	<2.9	<2.9
Fonofos	<1.0	<1.0	<0.30	<1.0	<1.0	<1.0	<1.0	<0.30	<0.30	<0.30	<0.30
Hexazinone	--	--	<50	--	--	--	--	<50	<50	<50	<50
Iprodione	--	--	<54	--	--	--	--	<54	<54	<54	<54
Isofenphos <sup>2</sup>	--	--	<0.34	--	--	--	--	<0.34	<0.34	<0.34	<0.34
Malathion	--	--	<2.7	--	--	--	--	<2.7	<2.7	<2.7	<2.7
Malathion, oxygen analog	--	--	<3.0	--	--	--	--	<3.0	<3.0	<3.0	<3.0
Metalaxyl	--	--	<2.9	--	--	--	--	<2.9	<2.9	<2.9	<2.9
Methidathion	--	--	<0.58	--	--	--	--	<0.58	<0.58	<0.58	<0.58
Metolachlor	--	--	<0.60	--	--	--	--	<0.60	<0.60	<0.60	<0.60
Metribuzin	--	--	<2.6	--	--	--	--	<2.6	<2.6	<2.6	<2.6
Myclobutanil	--	--	<0.80	--	--	--	--	<0.80	<0.80	<0.80	<0.80
1-Naphthol	--	--	<8.8	--	--	--	--	<8.8	<8.8	<8.8	<8.8
Parathion-methyl	--	--	<1.5	--	--	--	--	<1.5	<1.5	<1.5	<1.5
Parathion-methyl, oxygen analog	--	--	<3.0	--	--	--	--	<3.0	<3.0	<3.0	<3.0
Pendimethalin	<2.2	<2.2	<2.2	<2.2	<2.2	<2.2	<2.2	<2.2	<2.2	<20	<20
<i>cis</i> -Permethrin	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<5.8	<0.60
Phorate	--	--	<1.1	--	--	--	--	<1.1	<1.1	<1.1	<1.1
Phorate oxygen analog	--	--	<11	--	--	--	--	<11	<11	<11	<11
Prometon	--	--	<1.0	--	--	--	--	<1.0	<1.0	<1.0	<1.0
Prometryn	--	--	<0.54	--	--	--	--	<0.54	<0.54	<0.54	<0.54
Propyzamide	<0.40	<0.40	<0.40	<0.40	<0.40	<0.40	<0.40	<0.40	<0.40	<0.40	<0.40
Simazine	--	--	<0.50	--	--	--	--	<0.50	<0.50	<0.50	<0.50
Tebuthiuron	--	--	<1.6	--	--	--	--	<1.6	<1.6	<1.6	<1.6
Terbufos	--	--	<1.7	--	--	--	--	<1.7	<1.7	<1.7	<1.7
Terbufos oxygen analog sulfone	--	--	<6.8	--	--	--	--	<6.8	<6.8	<6.8	<6.8
Terbutylazine	--	--	<1.0	--	--	--	--	<1.0	<1.0	<1.0	<1.0
Trifluralin	<0.90	<0.90	<0.90	<0.90	<0.90	<0.90	<0.90	<0.90	<0.90	<0.90	<0.90
$\alpha$ -HCH- <i>d6</i> surrogate, % recovery	16	27	32	58	20	44	16	28	47	60	61
Diazinon- <i>d10</i> surrogate, % recovery	ns	ns	55	ns	ns	ns	ns	43	48	89	91
Isofenphos surrogate, % recovery <sup>2</sup>	25	28	ns	128	43	130	34	ns	ns	ns	ns
Sample volume, liters	9.7	7.4	5.0	9.5	3.7	9.6	11.8	15.3	11.3	18.2	13.9

<sup>1</sup>2002 samples initially prepared using OCC method and analyzed by GC/ECD. Extract subsequently analyzed for CUPs by GC/EIMS.

<sup>2</sup>Isofenphos was a surrogate compound for 2002 samples but an analyte for 2003 sample.

20 Organochlorine Compounds and Current-Use Pesticides in Snow and Lake Sediment, 2002–03

**Table 5.** Concentrations of organohalogen compounds analyzed by gas chromatography/electron-capture negative ion mass spectrometry in field blanks and replicate snow samples collected in 2003.

[Environ, environmental sample; Repl, replicate sample; <, less than; E, estimated concentration; %, percent; concentrations in nanograms per liter; shaded cells denote detectable concentrations; PCB, polychlorinated biphenyls; PBDE, polybrominated diphenyl ethers]

Compound	Blank	Loch Vale Forest		Lake Irene Meadow	
	Field	Environ	Repl	Environ	Repl
Aldrin	<0.50	<0.50	<0.50	<0.50	<0.50
Chlorpyrifos	<0.29	<0.10	<0.10	<0.081	<0.10
<i>cis</i> -Chlordane	<0.13	<0.13	<0.13	<0.13	<0.13
<i>trans</i> -Chlordane	<0.15	<0.15	<0.15	<0.15	<0.15
Chlorothalonil	<1.0	E1.59	E2.56	E1.37	E1.44
Dacthal (DCPA)	<0.34	0.68	1.60	1.58	2.54
<i>o,p'</i> -DDD	<1.0	<1.0	<1.0	<1.0	<1.0
<i>o,p'</i> -DDE	<0.50	<0.50	<0.50	<0.50	<0.50
<i>p,p'</i> -DDE	<2.0	<2.0	<2.0	<2.0	<2.0
Dieldrin	<0.40	<0.40	<0.40	E0.22	<0.40
Endosulfan I	<0.07	0.27	0.75	0.79	0.80
Endosulfan II	<0.07	0.13	0.31	0.19	0.26
Endosulfan sulfate	<0.13	0.15	0.23	0.14	0.17
Endrin	<0.50	<0.50	<0.50	<0.50	<0.50
Endrin aldehyde	<0.50	<0.50	<0.50	<0.50	<0.50
Endrin ketone	<2.0	<2.0	<2.0	<2.0	<2.0
Fipronil	<0.07	<0.07	<0.07	<0.07	<0.07
Fipronil sulfide	<0.03	<0.03	<0.03	<0.03	<0.03
Fipronil sulfone	<0.07	<0.07	<0.07	<0.07	<0.07
Fipronil, desulfinyl	<0.26	<0.12	<0.12	<0.07	<0.12
Fipronil amide, desulfinyl	<0.31	<0.31	<0.31	<0.31	<0.31
$\alpha$ -HCH	<0.50	<0.50	<0.50	<0.50	<0.50
$\delta$ -HCH	<0.50	<0.50	<0.50	<0.50	<0.50
$\gamma$ -HCH (Lindane)	<0.25	<0.25	<0.25	<0.25	<0.25
Heptachlor	<1.0	<1.0	<1.0	<1.0	<1.0
Heptachlor epoxide	<0.13	<0.13	<0.13	<0.13	<0.13
Isodrin	<0.50	<0.50	<0.50	<0.50	<0.50
Mirex	<0.25	<0.25	<0.25	<0.25	<0.25
<i>cis</i> -Nonachlor	<0.07	<0.07	<0.07	<0.07	<0.07
<i>trans</i> -Nonachlor	<0.20	<0.20	<0.20	E0.14	<0.20
Octachlorostyrene	<0.07	<0.07	<0.07	<0.07	<0.07
Oxychlordane	<0.13	<0.13	<0.13	<0.13	<0.13
Pentachloroanisole (PCA)	<0.07	<0.07	<0.07	<0.07	<0.07
Trifluralin	<0.07	<0.07	<0.07	<0.07	<0.07
<i>PCB congeners</i>					
PCB 70	<1.0	<1.0	<1.0	<1.0	<1.0
PCB 101	<0.50	<0.50	<0.50	<0.50	<0.50
PCB 110	<0.25	<0.25	<0.25	<0.25	<0.25
PCB 118	0.71	<0.07	<0.07	<0.07	<0.07
PCB 138	0.68	<0.07	<0.07	<0.07	<0.07
PCB 146	<0.07	<0.07	<0.07	<0.07	<0.07
PCB 149	<0.50	<0.50	<0.50	<0.50	<0.50
PCB 151	<0.07	<0.07	<0.07	<0.07	<0.07
PCB 170	<0.07	<0.07	<0.07	<0.07	<0.07
PCB 174	<0.07	<0.07	<0.07	<0.07	<0.07
PCB 177	<0.07	<0.07	<0.07	<0.07	<0.07

**Table 5.** Concentrations of organohalogen compounds analyzed by gas chromatography/electron-capture negative ion mass spectrometry in field blanks and replicate snow samples collected in 2003.—Continued

[Environ, environmental sample; Repl, replicate sample; <, less than; E, estimated concentration; %, percent; concentrations in nanograms per liter; shaded cells denote detectable concentrations; PCB, polychlorinated biphenyls; PBDE, polybrominated diphenyl ethers]

Compound	Blank	Loch Vale Forest		Lake Irene Meadow	
	Field	Environ	Repl	Environ	Repl
<i>PCB congeners</i> —Continued					
PCB 180	<0.07	<0.07	<0.07	<0.07	<0.07
PCB 183	<0.07	<0.07	<0.07	<0.07	<0.07
PCB 187	<0.07	<0.07	<0.07	<0.07	<0.07
PCB 194	<0.07	<0.07	<0.07	<0.07	<0.07
PCB 206	<0.07	<0.07	<0.07	<0.07	<0.07
<i>PBDE congeners</i>					
PBDE 47	<0.80	<0.80	<0.80	<0.80	<0.80
PBDE 99	<0.40	<0.40	<0.40	<0.40	<0.40
PBDE 100	<0.35	<0.35	<0.35	<0.35	<0.35
PBDE 153	<0.13	<0.13	<0.13	<0.13	<0.13
PBDE 154	<0.03	<0.03	<0.03	<0.03	<0.03
<i>α-HCH-d6 surrogate, % recovery</i>	76	29	59	107	92
Sample volume, liters	5.0	15.3	11.3	18.2	13.9

percent differences in concentrations for the five detected compounds ranged from 1 to 94 percent with an average of 69 percent for the Loch Vale replicates and 21 percent for the Lake Irene replicates. The larger differences in concentrations between the Loch Vale replicates are partly explained by the larger difference in  $\alpha$ -HCH-*d6* surrogate recovery (67 RPD) between replicates compared to Lake Irene (16 RPD).

Field replicates were collected at two sites for lake sediment, and results for OCCs are presented in table 6. The only detected compound was DDE, which was detected in both replicate pairs. Ypsilon Lake replicates had excellent agreement. The difference between the Lake Haiyaha sediment replicates was fairly large (50 RPD); however, the concentrations were close to the reporting level of 0.5  $\mu\text{g}/\text{kg}$ .

## Laboratory Quality Control

Laboratory quality-control samples analyzed with the snow and sediment samples included reagent blanks, reagent spikes, and laboratory replicates. In addition, each environmental and quality-control sample was fortified with surrogate compounds before extraction to monitor performance of the sample-preparation process. Certified reference materials were included with sediments analyzed by the OCC method.

## Snow

Snow-sample analyses from each year included laboratory reagent blanks and reagent spikes. In 2002, the reagent spike was fortified with OCC-method compounds, and in 2003

**Table 6.** Concentrations of organochlorine compounds analyzed by gas chromatography/electron-capture detection in replicate sediment samples collected in 2003.

[Environ, environmental sample; Repl, replicate sample; <, less than; E, estimated concentration; %, percent; concentrations in micrograms per kilogram of sediment (dry weight); shaded cells denote detectable concentrations]

Compound	Lake Haiyaha		Ypsilon Lake	
	Environ	Repl	Environ	Repl
Aldrin	<1.5	<2.0	<5.5	<8.5
Chlordane, technical	<15	<20	<55	<85
<i>p,p'</i> -DDD	<1.5	<2.0	<9.0	<8.5
<i>p,p'</i> -DDE	E0.9	E1.5	E3.1	E3.1
<i>p,p'</i> -DDT	<1.5	<2.0	<5.5	<8.5
Dieldrin	<1.5	<2.0	<5.5	<8.5
Endosulfan I	<1.5	<2.0	<5.5	<8.5
Endrin	<1.5	<2.0	<5.5	<8.5
$\gamma$ -HCH (Lindane)	<1.5	<2.0	<5.5	<8.5
Heptachlor	<1.5	<2.0	<5.5	<8.5
Heptachlor epoxide	<1.5	<2.0	<5.5	<8.5
<i>p,p'</i> -Methoxychlor	<6.0	<8.0	<22.0	<34
Mirex	<1.5	<2.0	<5.5	<8.5
PCB Aroclor 1242	<15	<20	<55	<85
PCB Aroclor 1254	<15	<20	<55	<85
PCB Aroclor 1260	<15	<20	<55	<85
Toxaphene	<150	<200	<550	<850
<i>α</i> -HCH- <i>d6</i> surrogate, % recovery	73	103	76	100
Isodrin surrogate, % recovery	54	76	46	53
PCB 207 surrogate, % recovery	44	53	65	43

one reagent spike was fortified with OCC-method compounds and a second was fortified with CUP-method compounds. Results for blanks and reagent spikes analyzed by the CUP method are shown in table 7 and by the OHC instrumental analysis are shown in table 8. No compounds were detected in the laboratory blanks for either analysis (CUP and OHC) except for one detection of PCB 206 (0.27 ng/L) in the 2002 laboratory blank (table 8).

Recoveries of the 61 analytes fortified in the 2003 CUP spike that were determined by the CUP method ranged from 30 to 150 percent with a median of 95 percent (table 7), with compounds exhibiting greatest bias typically those with known performance limitations (Zaugg and others, 1995; Sandstrom and others, 2001). The 2002 OCC reagent spike contained only dieldrin and two surrogates of the compounds determined by the CUP method. Only 28 percent of dieldrin in the reagent spike was detected by the CUP analysis (GC/EIMS) (table 7) compared to 81 percent recovery by

the OCC method (GC/ECD) used in 2002 (results for snow samples not shown in report) indicating recoveries for samples extracted using the OCC method but analyzed for CUPs by GC/EIMS may be low. Median surrogate recoveries for all 2003 snow and quality-control samples determined by the CUP method (tables 4, 7, 13, 14) were 47 percent (range 15–96) for  $\alpha$ -HCH-*d6* and 64 percent (range 27–123) for diazinon-*d10*. Recoveries of 16 compounds and 3 surrogates in the 2002 OCC spike that were subsequently determined by the OHC instrumental analysis (GC/ECNIMS) ranged from 15 to 94 percent with a median of 52 percent (table 8). Recoveries were considerably lower than the average acceptable recovery-limits range (60–120 percent) for several compounds, particularly dieldrin (15 percent) and the isodrin surrogate (26 percent). Recoveries of 18 compounds and 1 surrogate in the 2003 OCC spike determined by the OHC instrumental analysis ranged from 21 to 122 percent with a median of 74 percent. Comparison of recoveries for the 2003

**Table 7.** Concentrations and percent recovery of current-use pesticides analyzed by gas chromatography/electron-impact mass spectrometry in laboratory blanks and reagent spikes analyzed with snow samples in 2002–03.

[<, less than; E, estimated concentration; --, not determined; %, percent; ng/L, nanogram per liter; ns, not in spike or surrogate; OCC, organochlorine compounds analyzed by gas chromatography/electron capture detection (GC/ECD); CUP, current-use pesticides analyzed by gas chromatography/electron-impact mass spectrometry (GC/EIMS)]

Compound	2002		2003		
	Laboratory blank (ng/L)	Reagent spike <sup>1</sup> (% recovery)	Laboratory blank (ng/L)	Reagent spike <sup>1</sup> (% recovery)	Reagent Spike <sup>2</sup> (% recovery)
Acetochlor	<0.60	ns	<0.60	ns	104
Alachlor	<13	ns	<8.0	ns	92
Atrazine	--	ns	<1.5	ns	86
Azinphos-methyl	--	ns	<5.0	ns	109
Azinphos-methyl, oxygen analog	--	ns	<11	ns	E44
Benfluralin	<1.0	ns	<1.0	ns	79
Carbaryl	--	ns	<4.1	ns	E114
2-Chloro-2,6-diethylacetanilide	--	ns	<0.50	ns	104
2-Chloro-4-isopropylamino-6-amino-s-triazine	--	ns	<0.60	ns	34
4-Chloro-2-methylphenol	--	ns	<0.56	ns	36
Chlorpyrifos	<0.50	ns	<0.50	ns	95
Chlorpyrifos, oxygen analog	--	ns	<5.6	ns	51
Cyfluthrin	--	ns	<2.7	ns	149
Cypermethrin	--	ns	<0.86	ns	137
Dacthal	<0.30	ns	<0.30	ns	83
Diazinon	<0.50	ns	<0.50	ns	89
Diazinon, oxygen analog	<0.60	ns	<0.60	43	69
3,4-Dichloroaniline	--	ns	<0.45	ns	69
Dichlorvos	--	ns	<1.2	ns	E62
Dicrotophos	--	ns	<8.4	ns	E53
Dieldrin	<0.90	28	<0.90	ns	69
2,6-Diethylaniline	<0.60	ns	<0.60	ns	40
Dimethoate	--	ns	<0.61	ns	71
Ethion	<0.40	ns	<0.40	ns	93

**Table 7.** Concentrations and percent recovery of current-use pesticides analyzed by gas chromatography/electron-impact mass spectrometry in laboratory blanks and reagent spikes analyzed with snow samples in 2002–03.—Continued

[<, less than; E, estimated concentration; --, not determined; %, percent; ng/L, nanogram per liter; ns, not in spike or surrogate; OCC, organochlorine compounds analyzed by gas chromatography/electron capture detection (GC/ECD); CUP, current-use pesticides analyzed by gas chromatography/electron-impact mass spectrometry (GC/EIMS)]

Compound	2002		2003		
	Laboratory blank (ng/L)	Reagent spike <sup>1</sup> (% recovery)	Laboratory blank (ng/L)	Reagent spike <sup>1</sup> (% recovery)	Reagent Spike <sup>2</sup> (% recovery)
Ethion monoxon	--	ns	<0.20	ns	131
2-Ethyl-6-methylaniline	<0.45	ns	<0.45	ns	30
Fenamiphos	--	ns	<2.9	ns	E147
Fenamiphos sulfone	--	ns	<4.9	ns	E124
Fenamiphos sulfoxide	--	ns	<3.9	ns	E114
Fipronil	--	ns	<1.6	ns	124
Fipronil sulfide	--	ns	<1.3	ns	100
Fipronil sulfone	--	ns	<2.4	ns	91
Fipronil, desulfinyl	--	ns	<1.2	ns	86
Fipronil amide, desulfinyl	--	ns	<2.9	ns	E120
Fonofos	<1.0	ns	<0.30	ns	74
Hexazinone	--	ns	<50	ns	110
Iprodione	--	ns	<54	ns	69
Isofenphos <sup>3</sup>	--	ns	<0.34	ns	105
Malathion	--	ns	<2.7	ns	113
Malathion, oxygen analog	--	ns	<3.0	ns	113
Metalaxyl	--	ns	<2.9	ns	100
Methidathion	--	ns	<0.58	ns	85
Metolachlor	--	ns	<0.60	ns	98
Metribuzin	--	ns	<2.6	ns	111
Myclobutanil	--	ns	<0.80	ns	135
1-Naphthol	--	ns	<8.8	ns	78
Parathion-methyl	--	ns	<1.5	ns	93
Parathion-methyl, oxygen analog	--	ns	<3.0	ns	106
Pendimethalin	<2.2	ns	<2.2	ns	132
<i>cis</i> -Permethrin	<0.60	ns	<0.60	ns	132
Phorate	--	ns	<1.1	ns	68
Phorate, oxygen analog	--	ns	<11	ns	E114
Prometon	--	ns	<1.0	ns	108
Prometryn	--	ns	<0.54	ns	107
Propyzamide	<0.40	ns	<0.40	ns	97
Simazine	--	ns	<0.50	ns	95
Tebuthiuron	--	ns	<1.6	ns	E150
Terbufos	--	ns	<1.7	ns	80
Terbufos oxygen analog sulfone	--	ns	<6.8	ns	102
Terbuthylazine	--	ns	<1.0	ns	89
Trifluralin	<0.90	ns	<0.90	ns	91
$\alpha$ -HCH- <i>d6</i> surrogate, % recovery	33	28	15	64	62
Diazinon- <i>d10</i> surrogate, % recovery	ns	ns	27	98	92
Isofenphos surrogate, % recovery <sup>3</sup>	34	53	ns	ns	ns

<sup>1</sup>Reagent spike fortified with OCC method compounds only.

<sup>2</sup>Reagent spike fortified with CUP method compounds only.

<sup>3</sup>Isofenphos was a surrogate compound for 2002 samples but an analyte for 2003 samples.

## 24 Organochlorine Compounds and Current-Use Pesticides in Snow and Lake Sediment, 2002–03

**Table 8.** Concentrations and percent recovery of organohalogen compounds analyzed by gas chromatography/electron-capture negative ion mass spectrometry in laboratory blanks and reagent spikes analyzed with snow samples in 2002–03.

[<, less than; --, not determined; %, percent; ng/L, nanogram per liter; ns, not in spike or surrogate; shaded cells denote detectable concentrations; OCC, organochlorine compounds analyzed by gas chromatography/electron capture detection (GC/ECD); CUP, current-use pesticides analyzed by gas chromatography/electron-impact mass spectrometry (GC/EIMS); PCB, polychlorinated biphenyls; PBDE, polybrominated diphenyl ethers]

Compound	2002		2003		
	Laboratory blank (ng/L)	Reagent spike <sup>1</sup> (% recovery)	Laboratory blank (ng/L)	Reagent spike <sup>1</sup> (% recovery)	Reagent spike <sup>2</sup> (% recovery)
Aldrin	<0.25	51	<0.50	21	ns
Chlorpyrifos	<0.03	ns	<0.29	ns	148
<i>cis</i> -Chlordane	<0.07	86	<0.13	81	ns
<i>trans</i> -Chlordane	<0.15	88	<0.15	69	ns
Chlorothalonil	<1.0	ns	<1.0	ns	ns
Dacthal (DCPA)	<0.03	ns	<0.34	ns	156
<i>o,p'</i> -DDD	<0.50	ns	<1.0	ns	ns
<i>o,p'</i> -DDE	<0.50	ns	<0.50	ns	ns
<i>p,p'</i> -DDE	<0.50	94	<2.0	89	154
Dieldrin	<0.25	15	<0.40	54	98
Endosulfan I	<0.07	43	<0.07	80	180
Endosulfan II	<0.07	43	<0.07	59	142
Endosulfan sulfate	--	--	<0.13	58	147
Endrin	<0.25	53	<0.50	82	ns
Endrin aldehyde	--	--	<0.50	122	ns
Endrin ketone	--	--	<2.0	44	ns
Fipronil	--	ns	<0.07	ns	60
Fipronil sulfide	--	ns	<0.03	ns	112
Fipronil sulfone	--	ns	<0.07	ns	94
Fipronil, desulfinyl	--	ns	<0.26	ns	160
Fipronil amide, desulfinyl	--	ns	<0.31	ns	57
$\alpha$ -HCH	<0.25	68	<0.50	102	169
$\delta$ -HCH	<0.50	81	<0.50	98	ns
$\gamma$ -HCH (Lindane)	<0.25	52	<0.25	82	177
Heptachlor	<0.50	30	<1.0	37	ns
Heptachlor epoxide	<0.13	25	<0.13	44	ns
Hexachlorobenzene (HCB)	<0.17	30	--	--	--
Isodrin <sup>3</sup>	--	--	<0.50	ns	ns
Mirex	<0.25	84	<0.25	37	ns
<i>cis</i> -Nonachlor	<0.07	ns	<0.07	ns	ns
<i>trans</i> -Nonachlor	<0.18	78	<0.20	69	ns
Octachlorostyrene	<0.07	ns	<0.07	ns	ns
Oxychlordane	<0.13	ns	<0.13	ns	ns
Pentachloroanisole (PCA)	<0.07	ns	<0.07	ns	ns
Trifluralin	<0.07	ns	<0.07	ns	77
<i>PCB congeners</i>					
PCB 70	<0.50	ns	<1.0	ns	ns
PCB 101	<0.25	ns	<0.50	ns	ns
PCB 110	<0.25	ns	<0.25	ns	ns
PCB 118	<0.24	ns	<0.07	ns	ns
PCB 138	<0.07	ns	<0.07	ns	ns
PCB 146	<0.07	ns	<0.07	ns	ns
PCB 149	<0.25	ns	<0.50	ns	ns

**Table 8.** Concentrations and percent recovery of organohalogen compounds analyzed by gas chromatography/electron-capture negative ion mass spectrometry in laboratory blanks and reagent spikes analyzed with snow samples in 2002–03.—Continued

[<, less than; --, not determined; %, percent; ng/L, nanogram per liter; ns, not in spike or surrogate; shaded cells denote detectable concentrations; OCC, organochlorine compounds analyzed by gas chromatography/electron capture detection (GC/ECD); CUP, current-use pesticides analyzed by gas chromatography/electron-impact mass spectrometry (GC/EIMS); PCB, polychlorinated biphenyls; PBDE, polybrominated diphenyl ethers]

Compound	2002		2003		
	Laboratory blank (ng/L)	Reagent spike <sup>1</sup> (% recovery)	Laboratory blank (ng/L)	Reagent spike <sup>1</sup> (% recovery)	Reagent spike <sup>2</sup> (% recovery)
<i>PCB congeners—Continued</i>					
PCB 151	<0.07	ns	<0.07	ns	ns
PCB 170	<0.07	ns	<0.07	ns	ns
PCB 174	<0.07	ns	<0.07	ns	ns
PCB 177	<0.07	ns	<0.07	ns	ns
PCB 180	<0.07	ns	<0.07	ns	ns
PCB 183	<0.07	ns	<0.07	ns	ns
PCB 187	<0.07	ns	<0.07	ns	ns
PCB 194	<0.07	ns	<0.07	ns	ns
PCB 206	0.27	ns	<0.07	ns	ns
<i>PBDE congeners</i>					
PBDE 47	<0.32	ns	<0.80	ns	ns
PBDE 99	<0.17	ns	<0.40	ns	ns
PBDE 100	<0.14	ns	<0.35	ns	ns
PBDE 153	<0.13	ns	<0.13	ns	ns
PBDE 154	<0.03	ns	<0.03	ns	ns
$\alpha$ -HCH- <i>d6</i> surrogate, % recovery	31	42	14	100	117
Isodrin surrogate, % recovery <sup>3</sup>	45	26	ns	ns	ns
PCB 207 surrogate, % recovery	21	82	ns	ns	ns

<sup>1</sup>Reagent spike fortified with OCC-method compounds only.

<sup>2</sup>Reagent spike fortified with CUP-method compounds only.

<sup>3</sup>Isodrin was a surrogate compound for 2002 samples but an analyte for 2003 samples.

CUP reagent spike determined by the CUP method (table 7) and the CUP reagent spike determined by the OHC instrumental analysis (table 8) reveals that recoveries by the CUP method (GC/EIMS) were closer to expected values and probably less biased than the OHC analysis (GC/ECD). This result is not unexpected because the CUP method was used to extract and analyze the reagent spike. The ratio of recoveries between the two analyses suggests that concentrations from the OHC instrumental analysis for samples processed by the CUP method may be biased high by as much as a factor of 2 for some analytes. Recoveries for 16 compounds in the 2003 CUP-method spike determined by the OHC instrumental analysis ranged from 57 to 180 percent with a median of 147 percent, with some recoveries nearly double those expected. Median surrogate recovery for all 2003 snow and quality-control samples determined by the OHC instrumental analysis (tables 8 and 15) was 59 percent (range 14–158) for  $\alpha$ -HCH-*d6* with lower recoveries resulting from preparation losses for several samples. The results presented in this section suggest that for compounds with low recovery percentages in reagent spikes or for snow samples with low surrogate

recoveries, the detection frequencies presented in this report may be biased low. Reported concentrations in field samples are not corrected using surrogate or spike recoveries.

## Lake Sediment

Sediment samples prepared by the OCC method were analyzed in three separate analytical runs including two in 2002 and one in 2003. Table 9 shows results for laboratory blanks and replicates analyzed with the sediment samples. No compounds were detected in any of the three laboratory blanks. For the replicate samples, the only detected compound was DDE, which was detected in both the environmental sample and laboratory replicate in each of the three replicate pairs (table 9). Relative percent differences between the replicate pairs were small (8–13 percent), indicating there was good consistency in identifying and quantifying this compound. Table 10 shows results for certified reference materials and reagent spikes analyzed with the sediment samples by the OCC method. The three certified reference materials analyzed (CRM 1944, CRM 362, and CRM D035) were within the



**Table 9.** Concentrations of organochlorine compounds analyzed by gas chromatography/electron-capture detection in laboratory blanks and replicates analyzed with sediment samples in three analytical runs during 2002–03.

[&lt;, less than; E, estimated concentration; --, not determined; %, percent; concentrations in micrograms per kilogram of sediment (dry weight); shaded cells denote detectable concentrations]

Compound	2002			2002			2003		
	Blank	Mirror Lake		Blank	Upper Bullhead Lake		Blank	Mokowanis Lake	
		Sample	Replicate		Sample	Replicate		Sample	Replicate
Aldrin	<0.5	<8.0	<8.0	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Chlordane, technical	<5.0	<80	<80	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
<i>cis</i> -Chlordane	--	--	--	--	--	--	<0.5	<0.5	<0.5
<i>trans</i> -Chlordane	--	--	--	--	--	--	<0.5	<0.5	<0.5
<i>p,p'</i> -DDD	<0.5	<8.0	<8.0	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
<i>p,p'</i> -DDE	<0.5	E0.96	E1.1	<0.5	E0.34	E0.37	<0.5	0.88	E1.0
<i>p,p'</i> -DDT	<0.5	<8.0	<8.0	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Dieldrin	<0.5	<8.0	<8.0	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Endosulfan I	<0.5	<8.0	<8.0	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Endrin	<0.5	<8.0	<8.0	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
$\gamma$ -HCH (Lindane)	<0.5	<8.0	<8.0	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Heptachlor	<0.5	<8.0	<8.0	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Heptachlor epoxide	<0.5	<8.0	<8.0	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
<i>p,p'</i> -Methoxychlor	<2.0	<32	<32	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0
Mirex	<0.5	<8.0	<8.0	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
<i>trans</i> -Nonachlor	--	--	--	--	--	--	<0.5	<0.5	<0.5
PCB Aroclor 1242	<5.0	<80	<80	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
PCB Aroclor 1254	<5.0	<80	<80	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
PCB Aroclor 1260	<5.0	<80	<80	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
Toxaphene	<50	<800	<800	<50	<50	<50	<50	<50	<50
$\alpha$ -HCH- <i>d6</i> surrogate, % recovery	78	72	78	104	102	110	78	101	105
Isodrin surrogate, % recovery	53	40	50	63	58	57	64	67	90
PCB 207 surrogate, % recovery	74	63	73	109	87	86	80	72	81

acceptable control limits, with the exception of heptachlor in CRM 362, which was just outside (41 percent) the control limits of 42–146 percent. Reagent spike recoveries also were within the analytical control limits in all three analytical runs with the exception of heptachlor in the second 2002 run (18 percent), which, similar to CRM 362, was just below the lower control limit of 25 percent. Median recoveries for the three surrogates, which were added to each of the environmental and quality-control samples (tables 6, 9, 10, 17, 18), were 91 percent (range 40–110) for  $\alpha$ -HCH-*d6*, 56 percent (range 40–90) for isodrin, and 69 percent (range 43–109) for PCB 207. All surrogate recoveries were within control limits with the exception of  $\alpha$ -HCH-*d6* in two of the replicate samples (table 9) that were slightly higher than the upper control limit of 102 percent for this surrogate.

Results for the laboratory blank and reagent spike for the CUP sediment method are shown in table 11 and for the OCH instrumental analysis are shown in table 12. No compounds were detected in the laboratory blanks for either analysis type (CUP and OCH). Median recovery of 63 compounds in the CUP reagent spike analyzed by the CUP method was 88 percent (range 11–156), with larger deviation from 100 percent

expected for compounds with concentrations permanently reported as estimated (table 3; Foreman and others, 2005). Recoveries of the 10 compounds in the OCC-method reagent spike analyzed by the OHC instrumental analysis ranged from 54 to 80 percent (table 12). Recoveries for the six compounds in the CUP-method reagent spike were similar, ranging from 63 to 102 percent. Median surrogate recoveries in all sediments and quality-control samples analyzed by the CUP sediment method (tables 11 and 19) were 59 percent (range 50–133) for  $\alpha$ -HCH-*d6* and 115 percent (range 75–124) for diazinon-*d10*, compared to the control limits of 28–121 percent for  $\alpha$ -HCH-*d6* and 37–142 percent for diazinon-*d10*. The median surrogate recovery in all samples analyzed by the OHC instrumental analysis (tables 12 and 20) was 60 percent (range 55–77) for  $\alpha$ -HCH-*d6*.

Although recoveries for surrogates or analytes in reagent spikes or reference materials were less than 100 percent in many cases, they generally were within acceptable ranges for these samples and, therefore, do not necessarily indicate a low bias in detection frequencies and concentrations for the environmental sediment samples.

**Table 10.** Percent recovery and analytical control limits of organochlorine compounds analyzed by gas chromatography/electron-capture detection in certified reference materials and laboratory reagent spikes analyzed with sediment samples in three analytical runs during 2002–03.

Compound	2002				2002				2003			
	CRM 1944	Control limits	Reagent spike	Control limits	CRM 362	Control limits	Reagent spike	Control limits	CRM D035	Control limits	Reagent spike	Control limits
Aldrin	ns	15–133	49	15–133	61	47–136	74	15–133	59	50–121	68	32–101
Chlordane, technical	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
<i>cis</i> -Chlordane	--	--	--	--	--	--	--	--	59	43–123	72	45–81
<i>trans</i> -Chlordane	--	--	--	--	--	--	--	--	62	46–122	67	46–84
<i>p,p'</i> -DDD	52	22–158	56	22–158	63	44–148	54	22–158	61	57–126	86	29–105
<i>p,p'</i> -DDE	44	34–140	79	34–140	69	51–133	92	34–140	64	49–126	90	51–120
<i>p,p'</i> -DDT	86	15–150	56	15–150	72	44–123	82	15–150	65	46–133	79	32–101
Dieldrin	ns	15–150	55	15–150	60	49–139	64	15–150	62	50–125	68	35–101
Endosulfan I	ns	25–94	42	25–94	89	38–122	62	25–94	51	40–119	63	32–86
Endrin	ns	33–133	59	33–133	86	60–142	76	33–133	78	55–130	77	39–105
$\gamma$ -HCH (Lindane)	ns	15–112	42	15–112	59	35–152	67	15–112	ns	ns	54	29–81
Heptachlor	ns	25–109	45	25–109	<b>41</b>	42–146	<b>18</b>	25–109	62	53–120	75	24–91
Heptachlor epoxide	ns	15–155	56	15–155	59	53–127	64	15–155	67	58–137	66	35–93
<i>p,p'</i> -Methoxychlor	ns	15–150	67	15–150	72	34–146	53	15–150	75	37–141	84	27–118
Mirex	ns	32–120	52	32–120	ns	ns	68	32–120	ns	ns	74	46–93
<i>trans</i> -Nonachlor	--	--	--	--	--	--	--	--	ns	ns	80	50–82
PCB as Aroclor 1242	ns	17–145	68	17–145	ns	ns	ns	ns	ns	ns	89	30–110
PCB as Aroclor 1254	ns	53–150	114	53–150	ns	ns	ns	ns	ns	ns	100	45–127
PCB as Aroclor 1260	ns	33–150	109	33–150	ns	ns	ns	ns	ns	ns	96	47–125
Toxaphene	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
$\alpha$ -HCH- <i>d6</i> surrogate, % recovery	58	15–102	40	15–102	100	15–102	88	15–102	84	15–102	80	15–102
Isodrin surrogate, % recovery	49	16–105	62	16–105	60	16–105	66	16–105	70	16–105	68	16–105
PCB 207 surrogate, % recovery	52	15–124	74	15–124	91	15–124	94	15–124	76	15–124	80	15–124

[ns, not in spike or surrogate; --, not determined; %, percent; CRM, certified reference material; values in bold outside control limits]

**Table 11.** Concentrations and percent recovery of current-use pesticides analyzed by gas chromatography/electron-impact mass spectrometry in laboratory blanks and reagent spikes analyzed with sediment samples in 2003.

[<, less than; %, percent; µg/kg, microgram per kilogram of sediment (dry weight); OCC, organochlorine compounds analyzed by gas chromatography/electron-capture detection (GC/ECD)]

Compound	Laboratory blank (µg/kg)	Reagent spike <sup>1</sup> (% recovery)
Acetochlor	<1	97
Alachlor	<1	87
Atrazine	<1	104
Azinphos-methyl	<5	120
Azinphos-methyl, oxygen analog	<30	105
Benfluralin	<1	65
Carbaryl	<2	96
2-Chloro-2,6-diethylacetanilide	<1	89
2-Chloro-4-isopropylamino-6-amino-s-triazine	<2	90
4-Chloro-2-methylphenol	<10	55
Chlorpyrifos	<1	86
Chlorpyrifos oxygen analog	<30	73
Cyfluthrin	<20	130
Cypermethrin	<20	134
Dacthal	<1.0	94
Diazinon	<1	91
Diazinon, oxygen analog	<5	73
3,4-Dichloroaniline	<75	40
Dichlorvos	<30	37
Dicrotophos	<3	75
Dieldrin	<2	99
2,6-Diethylaniline	<30	37
Dimethoate	<2	76
Ethion	<2	87
Ethion monoxon	<2	88
2-Ethyl-6-methylaniline	<30	37
Fenamiphos	<30	81
Fenamiphos sulfone	<10	107
Fenamiphos sulfoxide	<10	156
Fipronil	<1	104
Fipronil sulfide	<1	114
Fipronil sulfone	<1	108
Fipronil, desulfinyl	<1	96
Fipronil amide, desulfinyl	<1	114
Fonofos	<1	72
Fonofos oxygen analog	<5	85
Hexazinone	<44	113
Iprodione	<10	52
Isofenphos	<2	109
Malathion	<2	71
Malathion, oxygen analog	<5	56
Metalaxyl	<1	102
Methidathion	<2	101
Metolachlor	<1	93
Metribuzin	<4	82
Myclobutanil	<10	86
1-Naphthol	<10	11
Parathion-methyl	<2	82

**Table 11.**—Continued

Compound	Laboratory blank (µg/kg)	Reagent spike <sup>1</sup> (% recovery)
Parathion-methyl, oxygen analog	<5	76
Pendimethalin	<1	95
Phorate	<5	39
Phorate oxygen analog	<7	50
Prometon	<2	81
Prometryn	<2	92
<i>cis</i> -Permethrin	<5	142
<i>trans</i> -Permethrin	<5	112
Propyzamide	<2	77
Simazine	<2	96
Tebuthiuron	<3	74
Terbufos	<3	64
Terbufos-o-analogue sulfone	<5	93
Terbutylazine	<1	100
Trifluralin	<1	69
α-HCH- <i>d6</i> surrogate, % recovery	54	52
Diazinon- <i>d10</i> surrogate, % recovery	75	83

<sup>1</sup>Reagent spike fortified with OCC-method compounds only.

## Organochlorine Compounds and Current-Use Pesticides in Snow and Lake Sediment

### Snow

Because atmospheric deposition is the primary pathway by which pesticides enter remote high-elevation ecosystems in ROMO and GLAC, snow samples were collected to determine which pesticides are currently entering these systems and at what rates (loadings). Snow was selected as a sample medium because snowfall provides most of the annual precipitation in high-elevation areas. Snow sampling has an additional advantage in that a single full-depth snowpack sample collected at maximum accumulation represents the majority of the wet and dry deposition for the winter snowfall period. The snow-sampling sites for this study were selected along elevation gradients on each side (east-west) of the Continental Divide (fig. 7). In ROMO, snow was collected at eight sites that spanned an elevation range of about 660 m. At the Loch Vale and Lake Irene sites, samples were collected in adjacent forested and open (meadow) areas in 2003 to assess the influence of the forest canopy on pesticide concentrations and loading (Horstmann and McLaughlin, 1998). In GLAC, snow was collected at eight sites that spanned an elevation range of about 700 m. On average, the sites in ROMO were about 1,400 m higher than the sites in GLAC. Many of the sites sampled during this study are part of the Rocky Mountain snowpack network, which is a network of snowpack chemistry sites that have been monitored by the USGS since 1991 (Ingersoll and others, 2001).

**Table 12.** Concentrations and percent recovery of organohalogen compounds analyzed by gas chromatography/electron-capture negative ion mass spectrometry in laboratory blanks and reagent spikes analyzed with sediment samples in 2003.

[<, less than; %, percent; µg/kg, microgram per kilogram of sediment (dry weight); ns, not in spike or surrogate; OCC, organochlorine compounds analyzed by gas chromatography/electron-capture detection (GC/ECD); CUP, current-use pesticides analyzed by gas chromatography/electron-impact mass spectrometry (GC/EIMS); PCB, polychlorinated biphenyls; PBDE, polybrominated diphenyl ethers]

Compound	Laboratory blank (µg/kg)	Reagent spike <sup>1</sup> (% recovery)	Reagent spike <sup>2</sup> (% recovery)
Aldrin	<0.8	68	ns
Benfluralin	<0.1	ns	63
Chlorpyrifos	<0.1	ns	91
<i>cis</i> -Chlordane	<0.2	72	ns
<i>trans</i> -Chlordane	<0.1	67	ns
Dacthal (DCPA)	<0.27	nn	99
<i>o,p'</i> -DDD	<1.6	ns	ns
<i>o,p'</i> -DDE	<1.6	ns	ns
<i>o,p'</i> -DDT	<6.4	ns	ns
<i>o,p'</i> -DDD	<15	ns	ns
<i>o,p'</i> -DDE	<4.0	ns	ns
Dieldrin	<0.8	68	86
Endosulfan I	<0.1	63	ns
Endosulfan II	<0.1	ns	ns
Endosulfan sulfate	<0.2	ns	ns
Endrin	<0.8	77	ns
Endrin aldehyde	<0.8	ns	ns
Endrin ketone	<3.2	ns	ns
Fipronil	<0.4	ns	102
Fipronil sulfide	<6.4	ns	ns
Fipronil amide, desulfinyl	<1.6	ns	ns
α-HCH	<0.8	ns	ns
β-HCH	<1.6	ns	ns
δ-HCH	<0.8	ns	ns
γ-HCH (Lindane)	<0.8	54	ns
Heptachlor epoxide	<1.6	66	ns
Hexachlorobenzene (HCB)	4.7	ns	ns
Mirex	<0.8	74	ns
<i>cis</i> -Nonachlor	<0.2	ns	ns
<i>trans</i> -Nonachlor	<0.2	80	ns
Octachlorostyrene	<0.2	ns	ns
Oxychlordane	<1.6	ns	ns
Pentachloroanisole (PCA)	<0.1	ns	ns
Trifluralin	<0.1	ns	92
<i>PCB congeners</i>			
PCB 70	<1.6	ns	ns
PCB 101	<0.8	ns	ns
PCB 110	<0.8	ns	ns
PCB 118	<0.1	ns	ns

**Table 12.—Continued**

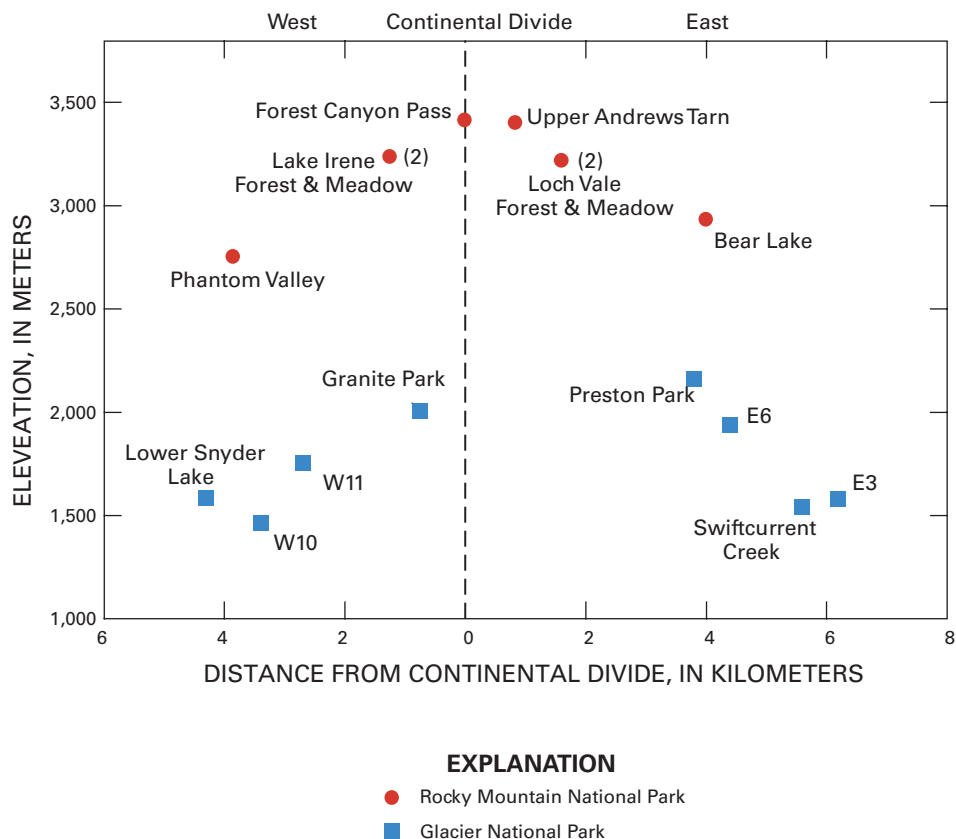
Compound	Laboratory blank (µg/kg)	Reagent spike <sup>1</sup> (% recovery)	Reagent spike <sup>2</sup> (% recovery)
<i>PCB congeners—Continued</i>			
PCB 138	<0.1	ns	ns
PCB 146	<0.1	ns	ns
PCB 149	<0.4	ns	ns
PCB 151	<0.1	ns	ns
PCB 170	<0.1	ns	ns
PCB 174	<0.1	ns	ns
PCB 177	<0.1	ns	ns
PCB 180	<0.1	ns	ns
PCB 183	<0.1	ns	ns
PCB 187	<0.1	ns	ns
PCB 194	<0.1	ns	ns
PCB 206	<0.1	ns	ns
<i>PBDE congeners</i>			
PBDE 47	<3.2	ns	ns
PBDE 99	<3.2	ns	ns
PBDE 100	<3.2	ns	ns
PBDE 153	<3.2	ns	ns
PBDE 154	<3.2	ns	ns
α-HCH- <i>d6</i> surrogate, % recovery	59	--	77

<sup>1</sup>Reagent spike fortified with OCC-method compounds only.

<sup>2</sup>Reagent spike fortified with CUP-method compounds only.

In 2002, snowfall was less than average in ROMO but greater than average in GLAC, and in 2003 snowfall was close to average in both parks. Maximum water content of the snowpack at the Bear Lake Snow Telemetry (SNOTEL) site in ROMO (fig. 3), which is operated by the Natural Resources Conservation Service, was 24 cm in 2002 and 63 cm in 2003 compared to the long-term (1971–2000) average of 50 cm (<http://www.wcc.nrcs.usda.gov/snow/>, accessed December 2005). In GLAC, maximum annual water content at the Flattop Mountain SNOTEL site (fig. 4) was 153 cm in 2002 and 112 cm in 2003 compared to the long-term (1971–2000) average of 118 cm. Snow depths at the sampling sites increased with elevation in both parks. In ROMO, snow depths in 2002 ranged from 70 cm at Phantom Valley to 327 cm at Upper Andrews Tarn. Snowpacks were typically deeper in GLAC, ranging from 184 cm at E3 to 370 cm at Granite Park. In both parks, snow depths on the east and west sides of the Continental Divide were comparable for sites at similar elevations.

Concentrations of pesticides and other compounds detected in snow samples are shown in tables 13–15, and the most frequently detected pesticides are shown in figure 8. Of the 66 compounds determined by the CUP method, only carbaryl, chlorpyrifos, and dacthal were detected in snow (tables 13–14). Dacthal was detected in all 19 of the snow samples analyzed, but carbaryl and chlorpyrifos were detected



**Figure 7.** Elevation and distance from Continental Divide of snow-sampling sites in Rocky Mountain National Park and Glacier National Park.

in only one sample each. Concentrations of all the detected compounds were very low, ranging from 0.27 to 2.2 ng/L. The concentrations of the detected pesticides in snow were not related to site elevation or location relative to the Continental Divide and were not notably different between meadow and forest sites, indicating that the presence of any fine canopy material in the 2003 samples had minimal or no influence on concentrations. Needles and other forest materials uptake organic contaminants (Reischl and others, 1987; Horstmann and McLaughlin, 1998), although their contribution, if any, to observed concentrations in 2002 snow samples cannot be distinguished. Concentrations were similar between the two parks with the exception of dacthal, which was slightly higher in ROMO compared to GLAC (fig. 9). For the organohalogen compounds, 10 of the 58 targeted compounds were detected in one or more snow samples including chlorpyrifos, chlorothalonil, dacthal, dieldrin, endosulfan I, endosulfan II, endosulfan sulfate, hexachlorobenzene (HCB), *trans*-nonachlor, and trifluralin (table 15). Three of these compounds—HCB, dieldrin, and *trans*-nonachlor—are organochlorine pesticides that have not been used commercially in the United States or Canada for several decades.

The pesticides most frequently detected in snow were endosulfan, dacthal, and chlorothalonil (fig. 8), which are all chlorinated pesticides that are registered for use in

North America. Endosulfan, which consists of two isomers (endosulfan I and endosulfan II), is the only chlorinated cyclodiene insecticide that is still in use in the United States (National Pesticide Information Retrieval System, <http://ppis.ceris.purdue.edu/htbin/epachem.com>, accessed February 2006). It is used on cotton and tobacco and on a wide variety of fruits and vegetables, particularly potatoes and apples. Endosulfan is highly toxic to fish and aquatic invertebrates (Johnson and Finley, 1980). Endosulfans were detected in all nine of the snow samples analyzed by GC/ECNIMS (table 15). Concentrations ranged from 0.20 to 1.06 ng/L for endosulfan I and 0.07 to 1.18 ng/L for endosulfan II. The highest concentrations of endosulfans were measured at Granite Park on the west side of GLAC. Both isomers were detected in all the snow samples, although concentrations of endosulfan I were as much as four times higher than endosulfan II. Higher concentrations of endosulfan I may reflect the composition of the technical mixture applied in agricultural areas, which contains a 7:3 mixture of endosulfan I to endosulfan II, as well as differences in physical properties (Shen and Wania, 2005). Endosulfan I is more volatile than endosulfan II and, thus, typically has higher atmospheric concentrations. However, endosulfan II has a lower Henry's law constant which favors its removal from the atmosphere by wet deposition and air-water exchange (Rice and others, 1997). Isomer conversion

**Table 13.** Concentrations of current-use pesticides analyzed by gas chromatography/electron-impact mass spectrometry in snow samples collected in Rocky Mountain National Park in 2002–03.

[<, less than; E, estimated concentration; --, not determined; %, percent; ns, not in spike or surrogate; concentrations in nanograms per liter; shaded cells denote detectable concentrations; OCC, organochlorine compounds analyzed by gas chromatography/electron-capture detection (GC/ECD); CUP, current-use pesticides analyzed by gas chromatography/electron-impact mass spectrometry (GC/EIMS)]

Compound	Bear Lake'	Loch Vale Forest'	Upper Andrews'	Phantom Valley'	Forest Canyon Pass'	Loch Vale Forest	Loch Vale Meadow	Bear Lake	Lake Irene Forest	Lake Irene Meadow
	04/03/2002	04/01/2002	04/01/2002	03/07/2002	03/29/2002	04/08/2003	04/07/2003	04/08/2003	04/01/2003	04/01/2003
Acetochlor	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60
Alachlor	<10.0	<10.0	<10.0	<20	<13	<8.0	<8.0	<8.0	<8.0	<8.0
Atrazine	--	--	--	--	--	<1.5	<1.5	<1.5	<1.5	<1.5
Azinphos-methyl	--	--	--	--	--	<8.7	<5.0	<5.0	<5.0	<5.0
Azinphos-methyl, oxygen analog	--	--	--	--	--	<11	<11	<11	<11	<11
Benfluralin	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Carbaryl	--	--	--	--	--	<4.1	0.82	<4.1	<4.1	<4.1
2-Chloro-2,6-diethylacetamide	--	--	--	--	--	<0.50	<0.50	<0.50	<0.50	<0.50
2-Chloro-4-isopropylamino-6-amino-s-triazine	--	--	--	--	--	<0.60	<0.60	<0.60	<0.60	<0.60
4-Chloro-2-methylphenol	--	--	--	--	--	<0.56	<0.56	<0.56	<0.56	<0.56
Chlorpyrifos	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50
Chlorpyrifos, oxygen analog	--	--	--	--	--	<5.6	<5.6	<5.6	<5.6	<5.6
Cyfluthrin	--	--	--	--	--	<2.7	<2.7	<2.7	<2.7	<2.7
Cypermethrin	--	--	--	--	--	<0.86	<0.86	<0.86	<0.86	<0.86
Dacthal	2.20	1.12	0.81	1.21	1.00	0.48	0.76	0.93	2.05	1.08
Diazinon	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50
Diazinon, oxygen analog	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60
3,4-Dichloroaniline	--	--	--	--	--	<0.45	<0.45	<0.45	<0.45	<0.45
Dichlorvos	--	--	--	--	--	<1.2	<1.2	<1.2	<1.2	<1.2
Dicrotophos	--	--	--	--	--	<8.4	<8.4	<8.4	<8.4	<8.4
Dieldrin	<0.90	<0.90	<0.90	<0.90	<0.90	<0.90	<0.90	<0.90	<0.90	<0.90
2,6-Diethylamine	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60
Dimethoate	--	--	--	--	--	<0.61	<0.61	<0.61	<0.61	<0.61
Ethion	<0.40	<0.40	<0.40	<0.40	<0.40	<0.40	<0.40	<0.40	<0.40	<0.40
Ethion monoxon	--	--	--	--	--	<0.20	<0.20	<0.20	<0.20	<0.20
2-Ethyl-6-methylamine	<0.45	<0.45	<0.45	<0.45	<0.45	<0.45	<0.45	<0.45	<0.45	<0.45
Fenamiphos	--	--	--	--	--	<2.9	<2.9	<2.9	<2.9	<2.9
Fenamiphos sulfone	--	--	--	--	--	<4.9	<4.9	<4.9	<4.9	<4.9
Fenamiphos sulfoxide	--	--	--	--	--	<3.9	<3.9	<3.9	<3.9	<3.9
Fipronil	--	--	--	--	--	<1.6	<1.6	<1.6	<1.6	<1.6
Fipronil sulfide	--	--	--	--	--	<1.3	<1.3	<1.3	<1.3	<1.3
Fipronil sulfone	--	--	--	--	--	<2.4	<2.4	<2.4	<2.4	<2.4
Fipronil, desulfinyl	--	--	--	--	--	<1.2	<1.2	<1.2	<1.2	<1.2
Fipronil amide, desulfinyl	--	--	--	--	--	<2.9	<2.9	<2.9	<2.9	<2.9

**Table 13.** Concentrations of current-use pesticides analyzed by gas chromatography/electron-impact mass spectrometry in snow samples collected in Rocky Mountain National Park in 2002–03.—Continued

[<, less than; E, estimated concentration; --, not determined; %, percent; ns, not in spike or surrogate; concentrations in nanograms per liter; shaded cells denote detectable concentrations; OCC, organochlorine compounds analyzed by gas chromatography/electron-capture detection (GC/ECD); CUP, current-use pesticides analyzed by gas chromatography/electron-impact mass spectrometry (GC/EIMS)]

Compound	Bear Lake'	Loch Vale Forest'	Upper Andrews'	Phantom Valley'	Forest Canyon Pass'	Loch Vale Forest	Loch Vale Meadow	Bear Lake	Lake Irene Forest	Lake Irene Meadow
	04/03/2002	04/01/2002	04/01/2002	03/07/2002	03/29/2002	04/08/2003	04/07/2003	04/08/2003	04/01/2003	04/01/2003
Fonofos	<1.0	<1.0	<1.0	<1.0	<1.0	<0.30	<0.30	<0.30	<0.30	<0.30
Hexazinone	--	--	--	--	--	<50	<50	<50	<50	<50
Iprodione	--	--	--	--	--	<54	<54	<54	<54	<54
Isofenphos <sup>2</sup>	--	--	--	--	--	<0.34	<0.34	<12	<0.34	<0.34
Malathion	--	--	--	--	--	<2.7	<2.7	<2.7	<2.7	<2.7
Malathion, oxygen analog	--	--	--	--	--	<3.0	<3.0	<3.0	<3.0	<3.0
Metaxyl	--	--	--	--	--	<2.9	<2.9	<2.9	<2.9	<2.9
Methidathion	--	--	--	--	--	<0.58	<0.58	<0.58	<0.58	<0.58
Metolachlor	--	--	--	--	--	<0.60	<0.60	<0.60	<0.60	<0.60
Metribuzin	--	--	--	--	--	<2.6	<2.6	<2.6	<2.6	<2.6
Myclobutanil	--	--	--	--	--	<0.80	<0.80	<0.80	<0.80	<0.80
1-Naphthol	--	--	--	--	--	<8.8	<8.8	<8.8	<8.8	<8.8
Parathion-methyl	--	--	--	--	--	<1.5	<1.5	<1.5	<1.5	<1.5
Parathion-methyl, oxygen analog	--	--	--	--	--	<3.0	<3.0	<3.0	<3.0	<3.0
Pendimethalin	<2.2	<2.2	<2.2	<2.2	<2.2	<2.2	<2.2	<2.2	<2.0	<2.0
cis-Permethrin	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60
Phorate	--	--	--	--	--	<1.1	<1.1	<1.1	<1.1	<1.1
Phorate oxygen analog	--	--	--	--	--	<11	<11	<11	<11	<11
Prometon	--	--	--	--	--	<1.0	<1.0	<1.0	<1.0	<1.0
Prometryn	--	--	--	--	--	<0.54	<0.54	<0.54	<0.54	<0.54
Propyzamide	<0.40	<0.40	<0.40	<0.40	<0.40	<0.40	<0.40	<0.40	<0.40	<0.40
Simazine	--	--	--	--	--	<0.50	<0.50	<0.50	<0.50	<0.50
Tebuthiuron	--	--	--	--	--	<1.6	<1.6	<1.6	<1.6	<1.6
Terbufos	--	--	--	--	--	<1.7	<1.7	<1.7	<1.7	<1.7
Terbufos oxygen analog sulfone	--	--	--	--	--	<6.8	<6.8	<6.8	<6.8	<6.8
Terbuthylazine	--	--	--	--	--	<1.0	<1.0	<1.0	<1.0	<1.0
Trifluralin	<0.90	<0.90	<0.90	<0.90	<0.90	<0.90	<0.90	<0.90	<0.90	<0.90
α-HCH-d6 surrogate, % recovery	58	27	29	38	24	28	31	46	96	60
Diazinon-d10 surrogate % recovery	ns	ns	ns	ns	ns	43	57	71	123	89
Isofenphos surrogate, % recovery <sup>2</sup>	128	72	55	133	62	ns	ns	ns	ns	ns
Sample volume, liters	9.5	10.3	11.4	6.3	10.6	15.3	13.4	14.9	16.8	18.2

<sup>1</sup>2002 samples initially prepared using OCC method and analyzed by GC/ECD. Extract subsequently analyzed for current-use pesticides by GC/EIMS.

<sup>2</sup>Isofenphos was a surrogate compound for 2002 samples but an analyte for 2003 samples.

**Table 14.** Concentrations of current-use pesticides analyzed by gas chromatography/electron-impact mass spectrometry in snow samples collected in Glacier National Park in 2002–03.

[<, less than; E, estimated concentration; --, not determined; ns, not in spike or surrogate; concentrations in nanograms per liter; shaded cells denote detectable concentrations; OCC, organochlorine compounds analyzed by gas chromatography/electron-capture detection (GC/ECD); CUP, current-use pesticides analyzed by gas chromatography/electron-impact mass spectrometry (GC/EIMS)]

Compound	Swiftcurrent Creek' 03/19/2002	E3' 03/12/2002	E6' 03/13/2002	Preston Park' 03/13/2002	W10' 03/12/2002	W11' 03/13/2002	Granite Park' 03/13/2002	Granite Park 04/08/2003	Lower Snyder 03/15/2003
Acetochlor	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60
Alachlor	<13	<13	<13	<13	<13	<13	<13	<8.0	<8.0
Atrazine	--	--	--	--	--	--	--	<1.5	<1.5
Azinphos-methyl	--	--	--	--	--	--	--	<5.0	<5.0
Azinphos-methyl, oxygen analog	--	--	--	--	--	--	--	<11	<11
Benfluralin	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Carbaryl	--	--	--	--	--	--	--	<4.1	<4.1
2-Chloro-2,6-diethylacetamide	--	--	--	--	--	--	--	<0.50	<0.50
2-Chloro-4-isopropylamino-6-amino-s-triazine	--	--	--	--	--	--	--	<0.60	<0.60
4-Chloro-2-methylphenol	--	--	--	--	--	--	--	<0.56	<0.56
Chlorpyrifos	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	2.06	<0.50
Chlorpyrifos, oxygen analog	--	--	--	--	--	--	--	E1.98	<5.6
Cyfluthrin	--	--	--	--	--	--	--	<2.7	<2.7
Cypermethrin	--	--	--	--	--	--	--	<0.86	<0.86
Dacthal	0.82	1.05	0.55	0.69	0.27	0.35	0.40	0.95	0.33
Diazinon	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50
Diazinon, oxygen analog	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60
3,4-Dichloroaniline	--	--	--	--	--	--	--	<0.45	<0.45
Dichlorvos	--	--	--	--	--	--	--	<1.2	<1.2
Dicrotophos	--	--	--	--	--	--	--	<8.4	<8.4
Dieldrin	<0.90	<0.90	<0.90	<0.90	<0.90	<0.90	<0.90	<0.90	<0.90
2,6-Diethylamine	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60
Dimethoate	--	--	--	--	--	--	--	<0.61	<0.61
Ethion	<0.40	<0.40	<0.40	<0.40	<0.40	<0.40	<0.40	<0.40	<0.40
Ethion monoxon	--	--	--	--	--	--	--	<0.20	<0.20
2-Ethyl-6-methylamine	<0.45	<0.45	<0.45	<0.45	<0.45	<0.45	<0.45	<0.45	<0.45
Fenamiphos	--	--	--	--	--	--	--	<2.9	<2.9
Fenamiphos sulfone	--	--	--	--	--	--	--	<4.9	<4.9
Fenamiphos sulfoxide	--	--	--	--	--	--	--	<3.9	<3.9
Fipronil	--	--	--	--	--	--	--	<1.6	<1.6
Fipronil sulfide	--	--	--	--	--	--	--	<1.3	<1.3
Fipronil sulfone	--	--	--	--	--	--	--	<2.4	<2.4
Fipronil, desulfinyl	--	--	--	--	--	--	--	<1.2	<1.2



**Table 14.** Concentrations of current-use pesticides analyzed by gas chromatography/electron-impact mass spectrometry in snow samples collected in Glacier National Park in 2002–03.—Continued

[<, less than; E, estimated concentration; --, not determined; %, percent; ns, not in spike or surrogate; concentrations in nanograms per liter; shaded cells denote detectable concentrations; OCC, organochlorine compounds analyzed by gas chromatography/electron-capture detection (GC/ECD); CUP, current-use pesticides analyzed by gas chromatography/electron-impact mass spectrometry (GC/EIMS)]

Compound	Swiftcurrent Creek' 03/19/2002	E3' 03/12/2002	E6' 03/13/2002	Preston Park' 03/13/2002	W10' 03/12/2002	W11' 03/13/2002	Granite Park' 03/13/2002	Granite Park 04/08/2003	Lower Snyder 03/15/2003
Fipronil amide, desulfinyl	--	--	--	--	--	--	--	<2.9	<2.9
Fonofos	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<0.30	<0.30
Hexazinone	--	--	--	--	--	--	--	<50	<50
Iprodione	--	--	--	--	--	--	--	<54	<54
Isofenphos <sup>2</sup>	--	--	--	--	--	--	--	<0.34	<0.34
Malathion	--	--	--	--	--	--	--	<2.7	<2.7
Malathion, oxygen analog	--	--	--	--	--	--	--	<3.0	<3.0
Metaxyl	--	--	--	--	--	--	--	<2.9	<2.9
Methidathion	--	--	--	--	--	--	--	<0.58	<0.58
Metolachlor	--	--	--	--	--	--	--	<0.60	<0.60
Metribuzin	--	--	--	--	--	--	--	<2.6	<2.6
Myclobutamil	--	--	--	--	--	--	--	<0.80	<0.80
1-Naphthol	--	--	--	--	--	--	--	<8.8	<8.8
Parathion-methyl, oxygen analog	--	--	--	--	--	--	--	<3.0	<3.0
Parathion-methyl	--	--	--	--	--	--	--	<1.5	<1.5
Pendimethalin	<2.2	<2.2	<2.2	<2.2	<2.2	<2.2	<2.2	<2.2	<2.2
cis-Permethrin	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60
Phorate	--	--	--	--	--	--	--	<1.1	<1.1
Phorate, oxygen analog	--	--	--	--	--	--	--	<11	<11
Prometon	--	--	--	--	--	--	--	<1.0	<1.0
Prometryn	--	--	--	--	--	--	--	<0.54	<0.54
Propyzamide	<0.40	<0.40	<0.40	<0.40	<0.40	<0.40	<0.40	<0.40	<0.40
Simazine	--	--	--	--	--	--	--	<0.50	<0.50
Tebuthiuron	--	--	--	--	--	--	--	<1.6	<1.6
Terbufos	--	--	--	--	--	--	--	<1.7	<1.7
Terbufos oxygen analog sulfone	--	--	--	--	--	--	--	<6.8	<6.8
Terbutylazine	--	--	--	--	--	--	--	<1.0	<1.0
Trifluralin	<0.90	<0.90	<0.90	<0.90	<0.90	<0.90	<0.90	<0.90	<0.90
$\alpha$ -HCH- <i>d6</i> surrogate, % recovery	60	51	24	54	16	20	36	42	28
Diazinon- <i>d10</i> surrogate, % recovery	ns	ns	ns	ns	ns	ns	ns	52	47
Isofenphos surrogate, % recovery <sup>2</sup>	87	86	80	103	34	50	61	ns	ns
Sample volume, liters	10.7	7.7	12.6	5.6	9.6	11.4	11.3	11.7	17.3

<sup>1</sup>2002 samples initially prepared using OCC method and analyzed by GC/ECD. Extract subsequently analyzed for current-use pesticides by GC/EIMS.

<sup>2</sup>Isofenphos was a surrogate compound for 2002 samples but an analyte for 2003 samples.

**Table 15.** Concentrations of organohalogen compounds analyzed by gas chromatography/electron-capture negative ion mass spectrometry in snow samples collected in Rocky Mountain National Park and Glacier National Park in 2002–03.

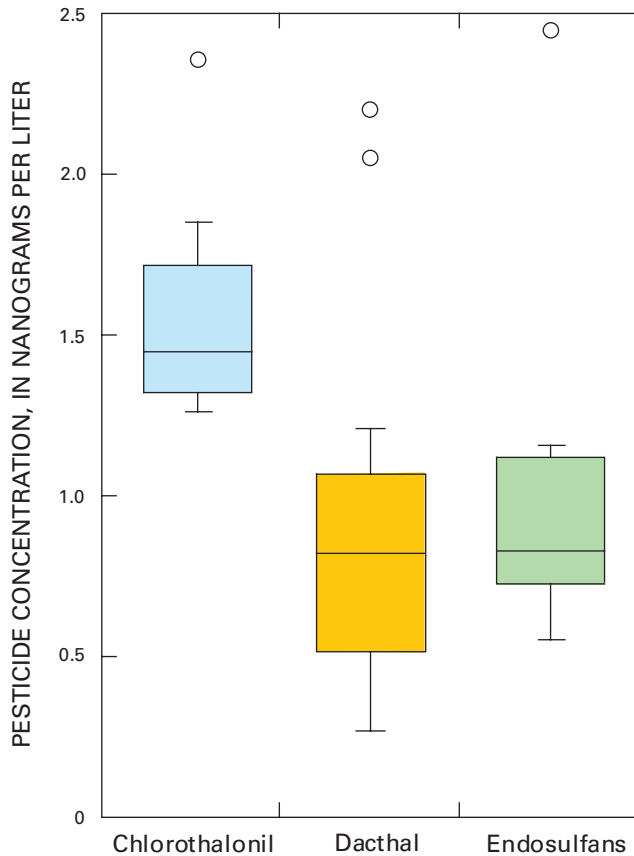
[&lt;, less than; E, estimated concentration; --, not determined; %, percent; ns, not in spike or surrogate; concentrations in nanograms per liter; shaded cells denote detectable concentrations]

Compound	Rocky Mountain National Park					Glacier National Park			
	Loch Vale Forest 04/01/2002	Upper Andrews 04/01/2002	Loch Vale Forest 04/08/2003	Loch Vale Meadow 04/07/2003	Bear Lake 04/08/2003	Lake Irene Forest 04/01/2003	Lake Irene Meadow 04/01/2003	Granite Park 04/08/2003	Lower Snyder 03/15/2003
Aldrin	<0.25	<0.25	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50
Chlorpyrifos	<0.03	<0.03	<0.10	<0.10	<0.10	<0.10	<0.08	2.11	<0.10
<i>cis</i> -Chlordane	<0.07	<0.07	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13
<i>trans</i> -Chlordane	<0.07	<0.07	<0.15	<0.15	<0.15	<0.15	<0.15	<0.15	<0.15
Chlorothalonil	E0.58	E0.51	E1.59	E1.26	E1.85	E2.36	E1.37	<1.0	<1.0
Dacthal (DCPA)	0.52	0.46	0.68	1.19	1.05	3.48	1.58	1.39	0.41
<i>o,p'</i> -DDD	<0.50	<0.50	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
<i>o,p'</i> -DDE	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50
<i>p,p'</i> -DDE	<0.50	<0.50	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0
Dieldrin	<0.10	<0.10	<0.40	<0.40	<0.40	<0.40	0.22	<0.40	<0.40
Endosulfan I	0.20	0.22	0.27	0.61	0.41	0.74	0.79	1.06	0.24
Endosulfan II	0.14	0.07	0.13	0.18	0.18	0.21	0.19	1.18	0.27
Endosulfan sulfate	--	--	0.15	0.15	0.16	0.21	0.14	0.21	0.18
Endrin	<0.25	<0.25	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50
Endrin aldehyde	--	--	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50
Endrin ketone	--	--	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0
Fipronil	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07
Fipronil sulfide	<0.13	<0.13	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
Fipronil sulfone	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07
Fipronil, desulfinyl	<0.07	<0.07	<0.12	<0.10	<0.12	<0.12	<0.07	<0.12	<0.12
Fipronil amide, desulfinyl	<0.20	<0.20	<0.31	<0.31	<0.31	<0.31	<0.31	<0.31	<0.31
$\alpha$ -HCH	<0.25	<0.25	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50
$\delta$ -HCH	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50
$\gamma$ -HCH (Lindane)	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25
Heptachlor	<0.50	<0.50	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Heptachlor epoxide	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13
Hexachlorobenzene (HCB)	E0.08	<0.08	--	--	--	--	--	--	--
Isodrin	<3.4	<3.4	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50
Mirex	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25
<i>cis</i> -Nonachlor	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07
<i>trans</i> -Nonachlor	<0.10	<0.10	<0.20	<0.20	<0.20	<0.20	E0.14	<0.20	<0.20

**Table 15.** Concentrations of organohalogen compounds analyzed by gas chromatography/electron-capture negative ion mass spectrometry in snow samples collected in Rocky Mountain National Park and Glacier National Park in 2002–03.—Continued

[<, less than; E, estimated concentration; --, not determined; %, percent; ns, not in spike or surrogate; concentrations in nanograms per liter; shaded cells denote detectable concentrations]

Compound	Rocky Mountain National Park						Glacier National Park		
	Loch Vale Forest 04/01/2002	Upper Andrews 04/01/2002	Loch Vale Forest 04/08/2003	Loch Vale Meadow 04/07/2003	Bear Lake 04/08/2003	Lake Irene Forest 04/01/2003	Lake Irene Meadow 04/01/2003	Granite Park 04/08/2003	Lower Snyder 03/15/2003
Octachlorostyrene	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07
Oxychlorodane	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13
Pentachloroisole (PCA)	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07
Trifluralin	E0.05	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07
<i>PCB congeners</i>									
PCB 70	<0.50	<0.50	<0.50	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
PCB 101	<0.25	<0.25	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50
PCB 110	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25
PCB 118	<0.10	<0.10	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07
PCB 138	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07
PCB 146	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07
PCB 149	<0.25	<0.25	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50
PCB 151	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07
PCB 170	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07
PCB 174	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07
PCB 177	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07
PCB 180	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07
PCB 183	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07
PCB 187	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07
PCB 194	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07
PCB 206	<0.27	<0.13	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07
<i>PBDE Congeners</i>									
PBDE 47	<0.78	<0.32	<0.80	<0.80	<0.80	<0.80	<0.80	<0.80	<0.80
PBDE 99	<0.39	<0.17	<0.40	<0.40	<0.40	<0.40	<0.40	<0.40	<0.40
PBDE 100	<0.34	<0.14	<0.35	<0.35	<0.35	<0.35	<0.35	<0.35	<0.35
PBDE 153	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13
PBDE 154	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
$\alpha$ -HCH-d6 surrogate, % recovery	29	34	29	44	52	158	107	44	35
Isodrin surrogate, % recovery	74	66	ns	ns	ns	ns	ns	ns	ns
PCB207 surrogate, % recovery	67	43	ns	ns	ns	ns	ns	ns	ns
Sample volume, liters	10.3	11.4	15.3	13.4	14.9	16.8	18.2	11.7	17.3



**Figure 8.** Concentration ranges of most frequently detected pesticides in snow collected in Rocky Mountain National Park and Glacier National Park.

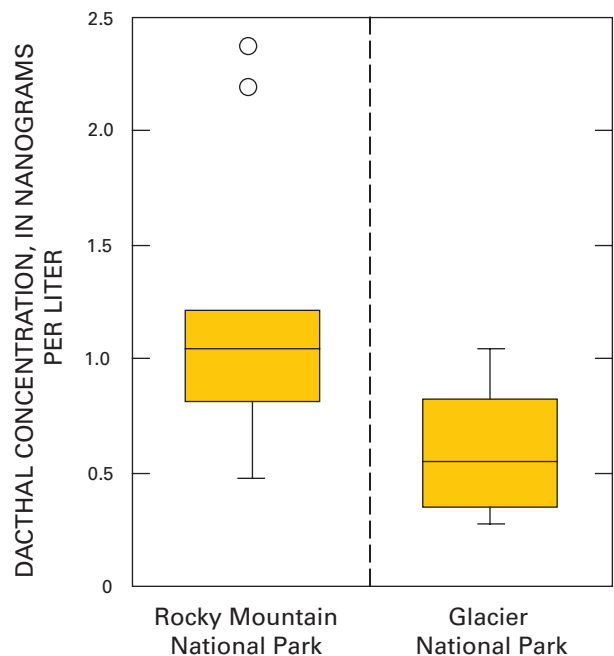
from endosulfan II to I also can occur (Schmidt and others, 2001). Endosulfan sulfate, which is a degradation product of endosulfan I and II, was detected in all seven of the 2003 samples in concentrations ranging from 0.14 to 0.21 ng/L. Endosulfan sulfate was not analyzed for in the 2002 samples.

Dacthal, also known as DCPA, is a pre-emergence herbicide used primarily on onions and broccoli as well as on sod farms, golf courses, and residential lawns (Kimbrough and Litke, 1997). Dacthal is only slightly toxic to aquatic organisms (Johnson and Finley, 1980; U.S. Environmental Protection Agency, 1988), and currently there are no established water-quality guidelines for this compound. All 19 snow samples collected during the study were analyzed for dacthal by GC/EIMS (tables 13–14). Nine of the 19 samples also were analyzed for dacthal by GC/ECNIMS (table 15). Dacthal was detected in all 19 samples by GC/EIMS and all 9 samples by GC/ECNIMS. Comparison between the GC/ECNIMS and GC/EIMS concentrations showed good correlation ( $r^2 = 0.95$ ), although the GC/ECNIMS concentrations tended to be about 30 percent higher than the GC/EIMS concentrations. Recovery of dacthal in the reagent spike by GC/EIMS was 83 percent (table 7), indicating the GC/EIMS values are reasonable. Recovery of dacthal in the reagent spike by GC/ECNIMS was 156 percent, however, which may indicate the GC/ECNIMS

concentrations are biased high (table 8). Dacthal concentrations in snow samples analyzed by GC/EIMS ranged from 0.27 to 2.2 ng/L, and the highest concentration was measured at Bear Lake (2002) on the east side of ROMO (table 13–14). The mono- and di-acid degradates of dacthal were not determined by the methods used in this study.

Chlorothalonil is a broad-spectrum organochlorine fungicide that is used on a variety of fruit and vegetable crops but most commonly on potatoes and peanuts. It also has nonagricultural uses on golf courses and in nurseries and as a fungicide in paints, grouts, and other building products. Chlorothalonil is highly toxic to aquatic organisms in laboratory studies; however, it does not have the high degree of persistence in the environment that is typical of many other chlorinated pesticides (<http://www.epa.gov/oppfead1/endanger/effects/#chlorothalonil>, accessed December 2005). Chlorothalonil was detected in seven of the nine snow samples analyzed by GC/ECNIMS (table 15). The estimated concentrations ranged from 0.51 to 2.36 ng/L, which generally were higher than concentrations of other detected compounds in snow (fig. 8). Interestingly, only snow from ROMO had detectable concentrations of chlorothalonil, although only two samples from GLAC were analyzed for the compound so the results may not be representative. Concentrations of chlorothalonil in snow were 1–2 orders of magnitude lower than the freshwater aquatic-life criterion of 0.18  $\mu\text{g/L}$  (table 3).

Because the snow-sampling sites are remote and pesticide usage in the parks is minimal, the most reasonable source for endosulfan, dacthal, and chlorothalonil is regional to long-range atmospheric transport and subsequent wet and



**Figure 9.** Comparison of dacthal concentrations in snow between Rocky Mountain National Park and Glacier National Park.

dry deposition to the snowpack. Based on air concentrations as measured by passive air samplers, Shen and others (2005) estimated that endosulfan I has a characteristic travel distance (or “half distance” analogous to half-life) of about 650 km or more in air. This travel distance indicates agricultural areas adjacent to ROMO and GLAC are the mostly likely source of endosulfans in snow. This is consistent with pesticide usage data, which shows heavy use of endosulfan in central Washington primarily for fruit, and moderate use in north-eastern and south-central Colorado, primarily for potatoes (fig. 10). Observations of endosulfans in high arctic air and snow (Gregor and Gummer, 1989; Patton and others, 1989; Chernyak and others, 1996; Shen and others, 2005) indicate that some endosulfans might come from long-range transport to the parks.

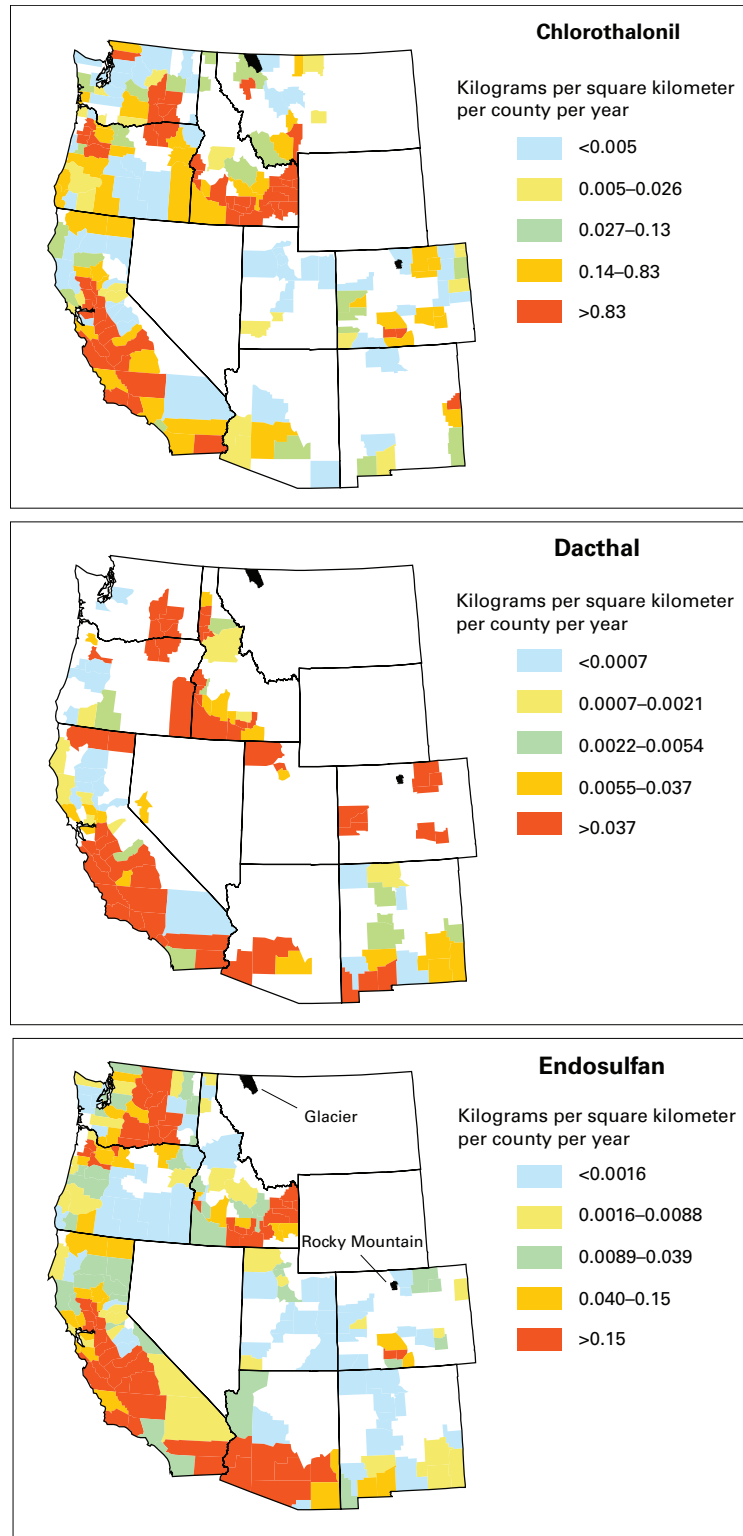
Dacthal also has properties that give it the potential for long-range atmospheric transport (Muir and others, 2004). It has been detected in air and rain samples collected at sites along the Great Lakes (James and Hites, 1999; Foreman and others, 2000) and in a watershed in southern Manitoba, Canada, distant from sources (Rawn and Muir, 1999), as well as in air samples from Cheeka Peak Observatory in Oregon (Killin and others, 2004), indicating that dacthal can be transported by air currents over regional to long distances. On the basis of empirical models, Muir and others (2004) determined that dacthal had a significantly greater potential for long-range transport than other commonly used current-use pesticides. Similar to endosulfan, the most likely source of dacthal in ROMO is in eastern Colorado (fig. 10), where it is among the 10 most commonly used agricultural herbicides on irrigated land and primarily is used for the cultivation of onions (Kimbrough and Litke, 1997). Usage around GLAC is heaviest in agricultural areas of the Idaho panhandle and in south-eastern Washington (fig. 10) where it also is used predominantly on onions (<http://www.ncfap.org/database/default.htm>, accessed December 2005). As noted previously, dacthal concentrations in snow from ROMO were slightly higher than in snow from GLAC (fig. 9). This pattern may reflect closer proximity of agricultural areas in eastern Colorado to ROMO compared to agricultural areas in Washington and Idaho, which are located farther to the west and south of GLAC.

The long-range transport characteristics of chlorothalonil are not well understood, in part because its analytical determination is challenging (Mackay and others, 1997). Chernyak and others (1996) reported concentrations in fog and seawater samples collected in the Bering and Chukchi Seas, indicating long-range atmospheric transport. McConnell and others (1998) detected chlorothalonil in snow and rain samples collected in Sequoia National Park and the Lake Tahoe Basin. It also has been detected in air samples from sites on the Great Lakes (James and Hites, 1999), at Cheeka Peak, Oregon (Killin and others, 2004), and on the Chesapeake Bay (Harman-Fetcho and others, 2000). The presence of this compound in ROMO snow indicates that it is transported at least regionally in the atmosphere. Chlorothalonil was

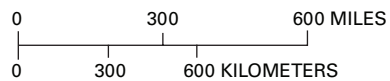
detected in all seven of the snow samples from ROMO and, similar to dacthal and endosulfan, probably was transported from agricultural and/or urban areas in the eastern part of the State, likely from use during potato cultivation where loss to the atmosphere can be substantial (White and others, 2006). Chlorothalonil was not detected in the two snow samples from GLAC despite the fact that there is reported use of the pesticide in areas adjacent to the park (fig. 10).

Of the banned or historical-use pesticides, only dieldrin, hexachlorobenzene (HCB), and *trans*-nonachlor were detected and only in one sample each. Dieldrin was used as a termiticide and as an insecticide primarily for cotton, corn, and fruit and was banned from use in the United States in the 1970s. HCB production, uses, and environmental fate and risk were recently reviewed by Jones (2005). HCB is a highly chlorinated compound that had varied applications. In agriculture, it was used as a fungicide as a seed dressing for onions, sorghum, and for crops such as wheat, barley, oats, and rye. It also was used as a wood preservative and in industrial applications, including production of chlorinated solvents, aromatics, and pesticides. In the United States, it has not been commercially produced since the late 1970s. However, HCB can be formed as a by-product in the production of some chlorinated compounds, including pesticides such as chlorothalonil, dacthal, and the chlorinated triazine herbicides including atrazine and simazine, which provides a continued, yet much reduced, source of HCB in North America (Jones, 2005). HCB has a very long residence time in the atmosphere that has allowed it to become widely distributed in the global atmosphere (Shen and others, 2005). HCB could not be determined in 2003 snow samples because it was not recovered from the graphitized carbon column used in the CUP method. *trans*-Nonachlor is one of the three major component congeners of technical chlordane, which was used as an insecticide and termiticide until the early 1980s when most of these uses were restricted in North America. Based on characteristic travel distances (Shen and others, 2005), sources of dieldrin and *trans*-nonachlor might be from regional or long-range transport. Limited detections of the banned compounds are possibly a reflection of decreasing atmospheric concentrations in North America (Cortes and others, 1998).

Atmospheric deposition rates of the most frequently detected pesticides were estimated for each park from snowpack concentrations and precipitation amount measured at the Bear Lake and Flattop Mountain SNOTEL sites. Average concentrations using data from both years for total endosulfans, dacthal, and chlorothalonil in ROMO were 0.78, 1.16, and 1.36, ng/L, respectively. Average concentrations of total endosulfans and dacthal in GLAC were 1.57 and 0.6 ng/L, respectively. Because chlorothalonil was not detected in GLAC snowpack samples, the concentration in snow was estimated as 0.5 ng/L, one-half the method reporting level. Using the long-term (1981–2005) annual (winter plus summer) precipitation amount at Bear Lake (89 cm) and assuming that average concentrations in snow are representative of precipitation over



Source: <http://ca.water.usgs.gov/pnsp>



**Figure 10.** Maps showing usage of chlorothalonil, dacthal, and endosulfan in the Western United States during 1997.

an entire year, annual deposition rates for total endosulfans, dacthal, and chlorothalonil in ROMO were estimated around 0.7, 1.0, and 1.2  $\mu\text{g}/\text{m}^2$ , respectively. Using long-term precipitation data at Flattop Mountain (196 cm), annual deposition for endosulfan, dacthal, and chlorothalonil in GLAC was estimated to be around 3.0, 1.2, and 1.0  $\mu\text{g}/\text{m}^2$ , respectively. The higher rates in GLAC compared to ROMO are largely a function of greater precipitation amounts in GLAC. These estimates of annual deposition are likely biased low on the basis of results from a recent study in ROMO that found pesticide concentrations in summer rain were substantially higher than in snow (Mast and others, 2003). For example, if the annual deposition rate of dacthal (the only pesticide measured in both studies) is recalculated for ROMO by using the average concentration in rain (6.1 ng/L) for the summer months (May–October), annual deposition increases to 3.0  $\mu\text{g}/\text{m}^2$  with 0.6  $\mu\text{g}/\text{m}^2$  deposited during winter and 2.4  $\mu\text{g}/\text{m}^2$  deposited during summer. This estimate is three times higher than the estimate based on snowpack concentrations alone and emphasizes the importance of year-round monitoring of precipitation chemistry to improve estimates of pesticide deposition rates to high-elevation ecosystems.

To place the snowpack results in some perspective, concentrations of selected current-use pesticides in this study are compared to precipitation data from other studies conducted in remote mountainous regions (table 16). In similar studies in ROMO, pesticides were measured in snow samples that were collected in spring of 2001 from four sites (Mast and others, 2001) and in rain samples collected near Bear Lake during summer of 2002 (Mast and others, 2003). Snow also was collected in ROMO in 2002–03 as part of the NPS Western Airborne Contaminants Assessment Project (WACAP). This program was initiated by the NPS to determine the risk to ecosystems and food webs in Western National Parks from the long-range transport of airborne contaminants (National Park Service, 2004). Concentrations of dacthal in snow were similar among the three studies in ROMO and varied by less than a factor of 4. By contrast, concentrations of dacthal in rain (3–9.3 ng/L) were as much as an order of magnitude higher than those measured in the snow (0.48–2.2 ng/L). Among the three ROMO studies, atrazine only was detected in snow collected during 2001 (Mast and others, 2001). Similar to dacthal, there were substantially higher atrazine concentrations in rain (14.7–60 ng/L) compared to snow (1.0–3.1 ng/L). Carbaryl was detected in nearly every rain sample in ROMO at concentrations as high as 95 ng/L but was detected in only one snow sample at a very low concentration (0.82 ng/L). The large difference in concentrations between snow and rain is not surprising considering that pesticide concentrations in air and precipitation generally are highest in spring and summer coinciding with pesticide application times and warmer temperatures that increase volatilization from soil and plant surfaces (Majewski and Capel, 1995; Carrera and others, 2002; Carlson and others, 2004). The organophosphorus insecticides (chlorpyrifos, diazinon, and malathion) were the most frequently

detected pesticides in rain and snow samples collected in the Sierra Nevada. This pattern is consistent with heavy usage of these pesticides in the Central Valley of California where pesticides are applied throughout the year (McConnell and others, 1998; Majewski and others, 2005).

For the organochlorine pesticides, endosulfan I was the most commonly detected compound in rain and snow from remote mountainous areas (table 16). Concentrations of endosulfan I in snow were similar among the three studies in ROMO and were similar to those measured in snow from the Canadian Rockies (Blais and others, 1998) and from a high-elevation site (1,920 m) in the Sierra Nevada (McConnell and others, 1998). Lindane ( $\gamma$ -HCH) was detected in the 2001 ROMO snow samples (0.6–1.1 ng/L) but not in any samples collected as part of the current study. Lindane also was detected in the 2002–03 samples collected as part of WACAP (National Park Service, 2005) but in concentrations nearly an order of magnitude lower than those measured in the 2001 ROMO snow. Blais and others (1998) detected several organochlorine compounds in snow collected along an elevation gradient in western Canada including HCH, heptachlorepoxide, dieldrin, DDT, and chlordane. Although the concentrations were very low (less than 1 ng/L), concentrations of most compounds tended to increase with elevation due to the effects of cold-condensation. In a similar study in mountainous regions of Europe, several organochlorine compounds were detected in snow, also at very low concentrations. For example, PCBs ranged from 0.20 to 2.2 ng/L and  $\gamma$ -HCH ranged from 0.02 to 1.1 ng/L (Carrera and others, 2001). Dieldrin, HCB, and *trans*-nonachlor were the only historical-use pesticides detected in snow samples collected as part of this study.

## Lake Sediment

Because sediments are recognized as a primary reservoir of organic contaminants to fish, surface sediments were collected to investigate occurrence and distribution of these compounds in park lakes and to determine if current levels of these compounds in lake sediment might pose a risk to aquatic organisms. The lakes selected for this study were high-elevation, oligotrophic lakes (fig. 11, table 2) that supported trout populations. In ROMO, the lowest lake was Fern Lake at 2,903 m and the highest was Timber Lake at 3,371 m. The lakes in GLAC were lower in elevation, ranging from 1,463 m at Akokala Lake to 1,926 m at Stoney Indian Lake. The smallest lake in ROMO was Fifth Lake at 1.8 ha, and the largest was Lake Nanita at 12.6 ha. The lakes in GLAC were slightly larger in area, ranging from 4.2 ha at Noname Lake to 15.2 ha at Slide Lake. The shallowest lake was Lake Janet in GLAC at 2 m, and the deepest was Black Lake in ROMO at 30 m.

All 11 surface-sediment samples from ROMO had low but detectable concentrations of DDE, which ranged from 0.62  $\mu\text{g}/\text{kg}$  (dry weight) in Fifth Lake to 15  $\mu\text{g}/\text{kg}$  in Lake

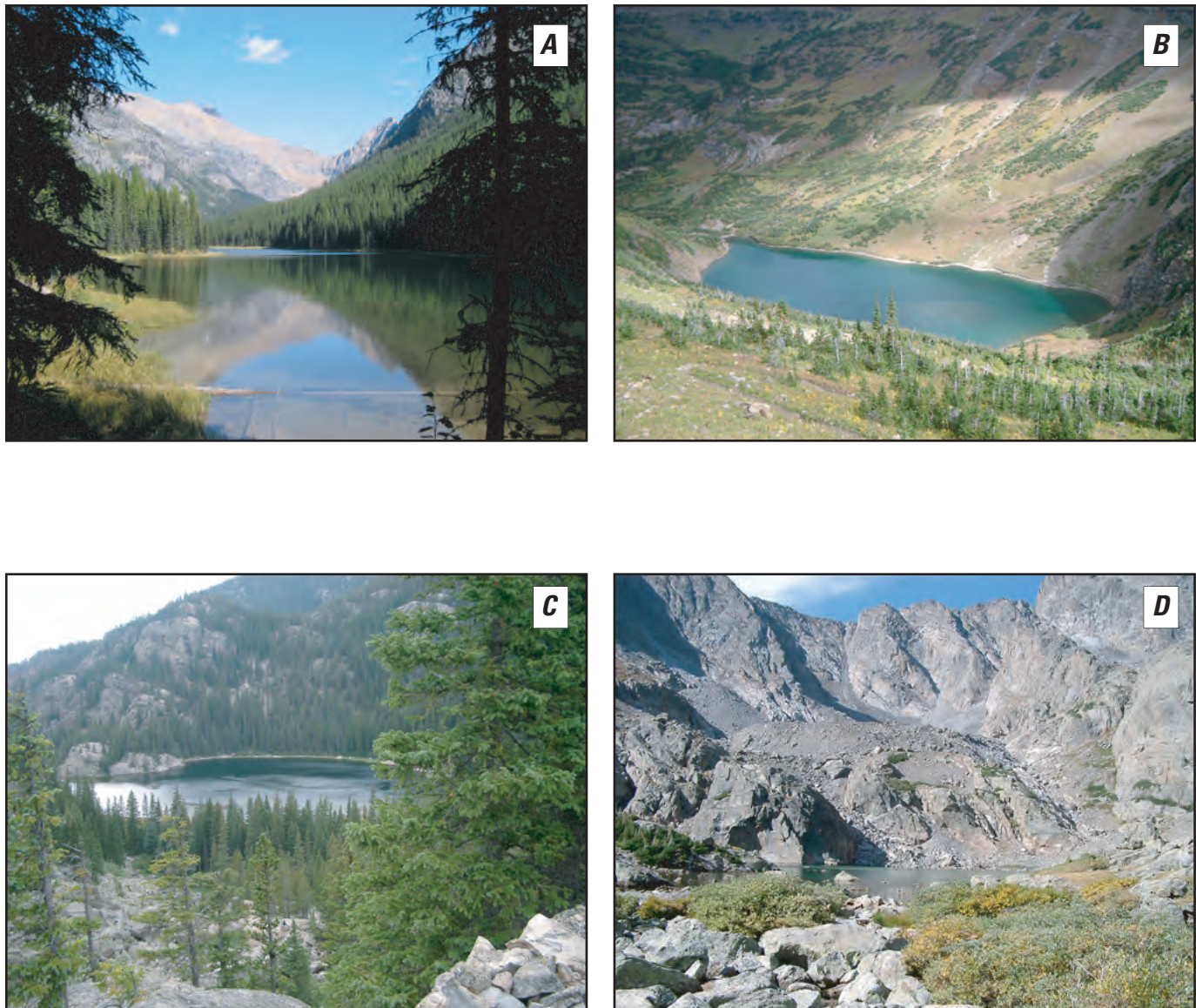
**Table 16.** Comparison of organic compound concentrations in snow and rain from remote mountainous regions.

[nd, not detected; --, not analyzed or not reported; ROMO, Rocky Mountain National Park; GLAC, Glacier National Park; concentrations in nanograms per liter; NPS, National Park Service]

Site	Type	Atrazine	Carbaryl	Chloro-thalonil	Chlor-pyrifos	Dacthal	Diazinon	Endo-sulfan I	HCB	$\alpha$ -HCH	$\gamma$ -HCH (Lindane)	Mala-thion	PCB	Reference
ROMO	Snow	nd	0.82 <sup>1</sup>	0.51–2.36	nd	0.48–2.2	nd	0.27–.79	0.08 <sup>1</sup>	nd	nd	nd	nd	this study
ROMO	Snow	1.0–3.1	nd	--	nd	0.8–1.1	nd	1.5–2.5	nd	nd	0.6–1.1	nd	--	Mast and others, 2001
ROMO	Snow	--	--	--	0.03 <sup>1</sup>	0.95–1.1	--	0.92–1.3	0.007 <sup>1</sup>	0.08–.14	0.07–.12	--	--	NPS, 2005
ROMO	Rain	14.7–60	7.9–95	--	nd	3–9.3	nd	--	--	--	nd	66 <sup>1</sup>	--	Mast and others, 2003
GLAC	Snow	nd	nd	nd	2.11 <sup>1</sup>	0.27–1.05	nd	0.24–1.06	nd	nd	nd	nd	nd	this study
Sierra Nevada	Snow/rain	--	--	0.66–85	0.30–13	--	3.7–19	0.93–6.5	--	--	0.39–1.87	3.6–24	--	McConnell and others, 1998
Canadian	Snow	--	--	--	--	--	--	0.03–0.5	--	0.06–0.78	0.05–0.35	--	0.30–2.17	Blais and others, 1998
Rockies	Snow	--	--	--	--	--	--	0.09–1.3	--	0.43–8.7	0.22–5.3	--	0.02–1.8	Gregor and Gummer, 1989
Canadian Arctic <sup>2</sup>	Snow	--	--	--	--	--	--	--	.025–0.22	--	0.02–1.1 <sup>3</sup>	--	0.2–2.2	Carrera and others, 2001
Europe	Snow/rain	--	--	--	--	--	--	0.03–45	0.03–0.22	0.30–0.48	1.5–5.6	--	0.32–2.8	Carrera and others, 2002

<sup>1</sup>Detected in only one sample.<sup>2</sup>Remote but nonmountainous area.<sup>3</sup>Sum of  $\alpha$ -HCH and  $\gamma$ -HCH.





**Figure 11.** Character of lakes sampled for sediment during the study including (A) Akokala Lake and (B) Stoney Indian Lake in Glacier National Park and (C) Lone Pine Lake and (D) Sky Pond in Rocky Mountain National Park.

Nanita (table 17). The relatively high concentration at Lake Nanita, however, is likely an analytical artifact related to the higher reporting levels for this sample, which resulted from a low sample dry weight. For this reason, the DDE value for Lake Nanita is not included in the following discussion. Surface sediment from 8 of the 11 lakes also had detectable DDD, but only Black Lake had a detectable concentration of DDT. In GLAC, 9 of the 10 lakes also had detectable concentrations of DDE in surface sediments. Only two lakes, Lake Janet and Stoney Indian Lake, had detectable concentrations of DDD and none of the sampled lakes had detectable DDT in surface sediment (table 18). The range of concentrations of DDD, which likely was formed in the anoxic lake sediments, was much narrower than DDE, which was formed either in oxidized surface sediments or was degraded before transport and burial. Sediment concentrations of DDE and DDD were

not related to lake elevation, surface area or depth, or lake location relative to the Continental Divide. The only notable spatial pattern was higher DDE and DDD concentrations in ROMO compared to GLAC (fig. 12), which might reflect closer proximity of ROMO to urban and agricultural areas compared to GLAC. Alternatively, the pattern in surface-sediment concentrations could simply be due to differences in sediment accumulation rates between the two parks. This latter explanation is plausible considering that GLAC is underlain by sedimentary bedrock types that are more erodible than the granitic and gneissic bedrock that underlies ROMO, which would result in lower sediment concentrations in GLAC. DDE and DDD concentrations in surface sediments of all lakes were below the probable effect concentration (PEC) of 31.3  $\mu\text{g}/\text{kg}$  for DDE and 28.0  $\mu\text{g}/\text{kg}$  for DDD. The PEC represents sediment concentrations above which harmful effects for benthic

**Table 17.** Concentrations of organochlorine compounds analyzed by gas chromatography/electron-capture detection in lake-sediment samples collected in Rocky Mountain National Park in 2002.

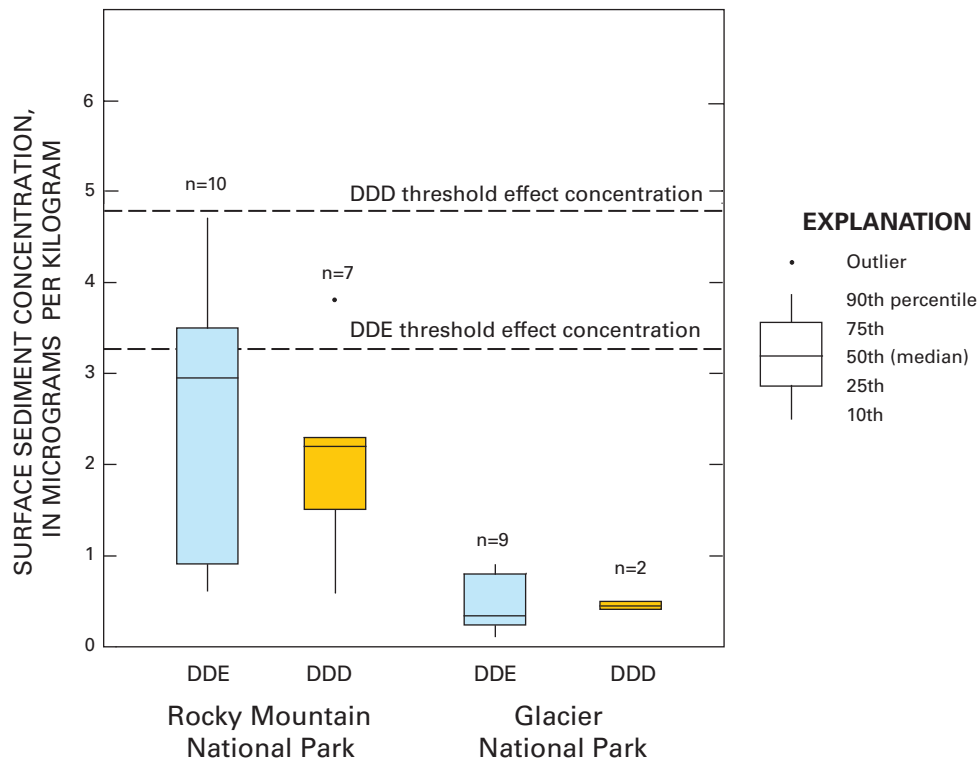
[<, less than; E, estimated concentration; --, not determined; %, percent; concentrations in micrograms per kilogram of sediment (dry weight); shaded cells denote detectable concentrations]

Compound	Black Lake	Fern Lake	Fifth Lake	Lake Haiyaha	Lake Nanita	Lone Pine Lake	Mirror Lake	Sandbeach Lake	Sky Pond	Timber Lake	Ypsilon Lake
	07/31/2003	07/11/2002	08/13/2002	08/13/2003	08/14/2002	08/12/2002	08/2/2002	07/22/2002	09/6/2002	08/1/2002	07/24/2003
Aldrin	<1.5	<2.5	<1.0	<1.5	<11	<3.5	<8.0	<1.5	<1.5	<4.0	<5.5
Chlordane, technical	<15	<25	<10	<15	<110	<35	<80	<15	<15	<40	<55
cis-Chlordane	<1.5	--	--	<1.5	--	--	--	--	--	--	<5.5
trans-Chlordane	<1.5	--	--	<1.5	--	--	--	--	--	--	<5.5
<i>p,p'</i> -DDD	2.20	E2.3	E0.60	<1.5	12	E2.3	<8.0	3.8	E0.80	E2.2	<9.0
<i>p,p'</i> -DDE	4.7	2.8	E0.62	E0.9	15	E3.1	E0.96	3.5	E 0.9	E3.5	E3.1
<i>p,p'</i> -DDT	E0.9	<2.5	<1.0	<1.5	<11	<3.5	<8.0	<1.5	<1.5	<4.0	<5.5
Dieldrin	<1.5	<2.5	<1.0	<1.5	<11	<3.5	<8.0	<1.5	<1.5	<4.0	<5.5
Endosulfan I	<1.5	<2.5	<1.0	<1.5	<11	<3.5	<8.0	<1.5	<1.5	<4.0	<5.5
Endrin	<1.5	<2.5	<1.0	<1.5	<11	<3.5	<8.0	<1.5	<1.5	<4.0	<5.5
$\gamma$ -HCH (Lindane)	<1.5	<2.5	<1.0	<1.5	<11	<3.5	<8.0	<1.5	<1.5	<4.0	<5.5
Heptachlor	<1.5	<2.5	<1.0	<1.5	<11	<3.5	<8.0	<1.5	<1.5	<4.0	<5.5
Heptachlor epoxide	<1.5	<2.5	<1.0	<1.5	<11	<3.5	<8.0	<1.5	<1.5	<4.0	<5.5
<i>p,p'</i> -Methoxychlor	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0
Mirex	<1.5	<2.5	<1.0	<1.5	<11	<3.5	<8.0	<1.5	<1.5	<4.0	<5.5
trans-Nonachlor	<1.5	--	--	<1.5	--	--	--	--	--	--	<5.5
PCB Aroclor 1242	<15	<25	<10	<15	<110	<35	<80	<15	<15	<4.0	<55
PCB Aroclor 1254	<15	<25	<10	<15	<110	<35	<80	<15	<15	<4.0	<55
PCB Aroclor 1260	<15	<25	<10	<15	<110	<35	<80	<15	<15	<4.0	<55
Toxaphene	<150	<250	<100	<150	<1100	<350	<800	<150	<150	<400	<550
$\alpha$ -HCH- <i>d6</i> surrogate, % recovery	101	74	78	107	63	76	72	80	77	72	100
Isodrin surrogate, % recovery	77	55	49	76	56	56	40	52	52	59	53
PCB 207 surrogate, % recovery	52	73	66	53	46	76	63	56	72	54	43

**Table 18.** Concentrations of organochlorine compounds analyzed by gas chromatography/electron-capture detection in lake-sediment samples collected in Glacier National Park in 2002–03.

[<, less than; E, estimated concentration; --, not determined; %, percent; concentrations in micrograms per kilogram of sediment (dry weight); shaded cells denote detectable concentrations]

Compound	Akokala Lake 09/20/2002	Atsina Lake 09/11/2003	Lake Janet 09/13/2003	Lower Snyder Lake 09/19/2002	Mokowanis Lake 09/10/2003	Noname Lake 09/18/2002	Redrock Lake 09/17/2002	Slide Lake 09/9/2003	Stoney Indian Lake 09/12/2003	Upper Bullhead Lake 09/17/2002
Aldrin	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<1.0	<0.5	<0.5
Chlordane, technical	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<10.0	<5.0	<5.0
<i>cis</i> -Chlordane	--	<0.5	<0.5	--	<0.5	--	--	<1.0	<0.5	--
<i>trans</i> -Chlordane	--	<0.5	<0.5	--	<0.5	--	--	<1.0	<0.5	--
<i>p,p'</i> -DDD	<0.5	<0.5	E0.5	<0.5	<0.5	<0.5	<0.5	<1.0	E0.4	<0.5
<i>p,p'</i> -DDE	E0.12	0.9	E0.7	E0.22	0.88	E0.23	E0.28	<1.0	0.8	E0.34
<i>p,p'</i> -DDT	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<1.0	<0.5	<0.5
Dieldrin	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<1.0	<0.5	<0.5
Endosulfan I	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<1.0	<0.5	<0.5
Endrin	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<1.0	<0.5	<0.5
$\gamma$ -HCH (Lindane)	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<1.0	<0.5	<0.5
Heptachlor	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<1.0	<0.5	<0.5
Heptachlor epoxide	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<1.0	<0.5	<0.5
<i>p,p'</i> -Methoxychlor	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<4.0	<2.0	<2.0
Mirex	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<1.0	<0.5	<0.5
<i>trans</i> -Nonachlor	--	<0.5	<0.5	--	<0.5	--	--	<1.0	<0.5	--
PCB Aroclor 1242	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<10.0	<5.0	<5.0
PCB Aroclor 1254	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<10.0	<5.0	<5.0
PCB Aroclor 1260	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<10.0	<5.0	<5.0
Toxaphene	<50	<50	<50	<50	<50	<50	<50	<100	<50	<50
$\alpha$ -HCH- <i>d6</i> surrogate, % recovery	73	108	96	90	101	92	89	91	98	102
Isodrin surrogate, % recovery	52	82	67	56	67	48	47	82	81	56
PCB 207 surrogate, % recovery	72	73	80	71	72	64	66	64	62	87



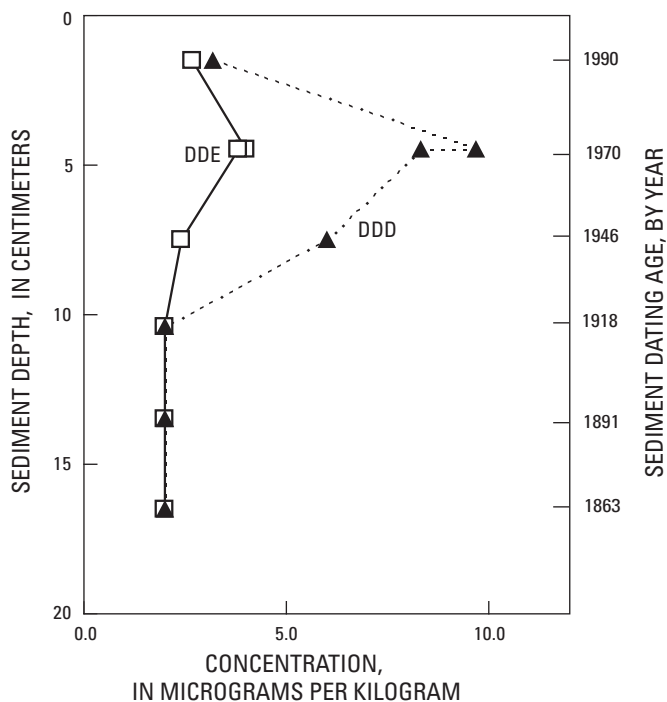
**Figure 12.** Range of DDD and DDE concentrations in surface sediments from lakes in Rocky Mountain National Park and Glacier National Park.

organisms are likely to be observed (MacDonald and others, 2000). Discounting Lake Nanita, three ROMO sediments were above the threshold effect concentrations (TEC) of 3.16  $\mu\text{g}/\text{kg}$  for DDE and no sediments exceeded the TEC of 4.88  $\mu\text{g}/\text{kg}$  for DDD. The TEC represents concentrations below which harmful effects for benthic organisms are unlikely to be observed (MacDonald and others, 2000). The other 14 organochlorine pesticides and 3 PCB aroclors (tables 17–18) and the 27 PCB congeners (2002 samples only, not shown in tables) analyzed by GC/ECD were not detected in any of the lake-sediment samples collected during the study.

DDE and DDD are degradation products of DDT, which is a well-documented, persistent organochlorine insecticide that has been banned from use in the United States since 1972. DDT and its degradates are of concern because they are endocrine-disrupting compounds that accumulate in the food chain and persist in the environment for long periods of time (Majewski and Capel, 1995; Tyler and others, 1998). Because the lakes in ROMO and GLAC are remote and there is no reported use of DDT in either park, the presence of DDE and DDD is likely the result of long-range atmospheric transport and subsequent wet and dry deposition to the lake and watershed. The source of these compounds in recent sediments (last 10 to 15 years) is unknown particularly because they have not been used in the United States since 1972. Recent air-quality studies in North America indicate DDT in the atmosphere is from an aged source such as volatilization from agricultural or forest soils that were contaminated in the past (Shen and

others, 2005). Another possibility is long-range transport from distant sources in Central America or Asia where some banned compounds are still in use (National Park Service, 2005; Shen and others, 2005). Neither DDT nor its degradates were detected in any of the snow samples collected during this study. This may be because the analytical detection limits in this study were not low enough to detect these compounds in snow. In a similar study, Usenko and others (2005) also did not detect DDT or its degradates in snow collected in ROMO in 2003, even though their detection limits were an order of magnitude lower than those in this study. The lack of detectable DDT in snow may indicate that atmospheric deposition of this compound may not be dominated by deposition to the snow-pack. Other potential atmospheric inputs of DDT are from wet and dry deposition to the lake and watershed during summer months and gas exchange between the air and lake water during the ice-free season (Blais and others, 2001).

Although DDD and DDE were detected in most of the surface sediments analyzed, the concentrations were very low and probably pose little threat to aquatic organisms. It is possible, however, that concentrations of these compounds may increase with sediment depth (and age) due to greater use in the past. Van Metre and Mahler (2005) found significant declines in sediment DDT, DDE, and PCB concentrations between 1970 and 2001 in sediment cores collected from lakes across the United States, reflecting the discontinued use of these compounds in North America over the past 3 decades. Although older sediments were not analyzed as



**Figure 13.** Concentrations of DDD and DDE in a lake-sediment core from Mills Lake in Rocky Mountain National Park (unpublished data, P. Van Metre, USGS).

part of this study, Mills Lake (2 km downstream from Black Lake in ROMO) was cored, dated, and analyzed for OCCs by the USGS in 1999 (P.C. Van Metre, U.S. Geological Survey, unpub. data, 2000). DDD and DDE concentrations in the Mills Lake sediment core show distinct increases with depth (fig. 13), and the highest concentrations were measured in sediments deposited during the 1970s (4.0 µg/kg DDE and 9.7 µg/kg DDD), which correlates with its ban from usage in North America in 1972. The results at Mills Lake indicate that concentrations of some OCCs measured in this study likely are higher at greater depths in undisturbed bottom sediments of lakes. These results also indicate that atmospheric deposition of DDT and possibly other banned organochlorine compounds to ROMO and other high-elevation parks has been in decline since the 1970s.

Lakes sampled in 2003, which included Black Lake, Lake Haiyaha, and Ypsilon Lake in ROMO and Atsina Lake, Lake Janet, Mokowanis Lake, Slide Lake, and Stoney Indian Lake in GLAC, also were analyzed for CUPs by GC/EIMS and OHCs by GC/ECNIMS. Only one CUP, dacthal, was detected in the lake sediments by GC/EIMS (table 19). Nine OHCs were detected by GC/ECNIMS: *trans*-chlordane, dacthal, DDE, endosulfan sulfate, HCB, *cis*-nonachlor, *trans*-nonachlor, and PCB congeners 180 and 187 (table 20).

Of these compounds, endosulfan sulfate was detected most frequently and occurred in six of the eight sediments analyzed including two lakes in ROMO and four lakes in GLAC. The highest concentrations of endosulfan sulfate

were measured in Black Lake (0.44 µg/kg) and Ypsilon Lake (1.2 µg/kg), both of which are on the east side of ROMO. Concentrations in the GLAC lakes were lower, ranging from 0.12 to 0.15 µg/kg. These results are consistent with the snow samples in which endosulfans (endosulfan I, endosulfan II, and endosulfan sulfate) were detected in nearly all of the snow samples, indicating that atmospheric deposition is the primary source of this pesticide entering park lakes. In contrast to snow, only the degradation product endosulfan sulfate was detected in sediments, indicating that the isomers (endosulfan I and II) are metabolized to endosulfan sulfate in the aquatic environment. Endosulfan sulfate typically is more persistent in aqueous environments than either of the parent isomers due to its longer half-life in water and soil (Peterson and Batley, 1993). Endosulfan in bed sediment has been shown to be toxic to aquatic invertebrates (Leonard and others, 2001), although currently there are no established sediment guidelines for aquatic life.

Dacthal was detected in four of the eight sediments analyzed by GC/ECNIMS: Black Lake in ROMO and Atsina Lake, Mokowanis Lake, and Stoney Indian Lake in GLAC (table 20). In three of these four samples, dacthal also was detected by GC/EIMS (table 19), confirming its presence in the sediments. Dacthal is considered a general hazard to fish, although there are no established guidelines for concentrations in sediment or surface water (Stephens and Deacon, 1997). As observed for endosulfans, dacthal was detected in nearly all of the snow samples, providing evidence that atmospheric deposition is the source of dacthal in lake sediments. Dacthal also was detected in summer precipitation samples collected on the east side of ROMO near Bear Lake (Mast and others, 2003), although at concentrations substantially higher than those measured in snow. Other current-use pesticides commonly detected in snow (this study) and rain (Mast and others, 2003) include atrazine, carbaryl, and chlorothalonil; however, none of these pesticides were detected in lake sediments. This pattern is reasonable because endosulfan and dacthal are more hydrophobic and persistent than many other current-use pesticides and therefore have a higher potential to accumulate in sediment and aquatic biota (Nowell and others, 1999).

Of the historical-use pesticides analyzed by GC/ECNIMS, components of chlordane (*trans*-chlordane, *cis*-nonachlor, *trans*-nonachlor) were detected most frequently, with at least one component occurring in four of the eight sediment samples analyzed. Technical chlordane was used as an insecticide and termiticide until the early 1980s when most of these uses were restricted in North America (<http://www.epa.gov/pbt/pubs/chlordane.htm>, accessed June 2006). Chlordane use in agriculture, primarily on corn, was discontinued in 1978. Commercial use of chlordane was banned in 1988 where it primarily was used in urban areas for control of termites, although it was still permitted for use by homeowners after 1988. The concentrations of the chlordane components detected in the lake sediments (0.10–1.0 µg/kg) were well below the threshold effect level of 3.24 µg/kg for chlordane reported by MacDonald and others (2000). Of the chlordane components, *trans*-nonachlor



**Table 19.** Concentrations of current-use pesticides analyzed by gas chromatography/electron-impact mass spectrometry in lake-sediment samples collected in Rocky Mountain National Park and Glacier National Park in 2003.—Continued

[<, less than; E, estimated concentration; %, percent; concentrations reported in micrograms per kilogram of sediment (dry weight); shaded cells denote detectable concentrations]

Compound	Rocky Mountain National Park					Glacier National Park				
	Black Lake 07/31/2003	Lake Haiyaha 08/13/2003	Ypsilon Lake 07/24/2003	Atsina Lake 09/11/2003	Lake Janet 09/13/2003	Mokowanis Lake 09/10/2003	Slide Lake 09/09/2003	Stoney Indian Lake 09/12/2003		
Fipronil sulfone	<1	<1	<1	<1	<1	<1	<1	<1		
Fipronil, desulfinyl	<1	<1	<1	<1	<1	<1	<1	<1		
Fipronil amide, desulfinyl	<1	<1	<1	<1	<1	<1	<1	<1		
Fonofos	<1	<1	<1	<1	<1	<1	<1	<1		
Fonofos, oxygen analog	<5	<5	<5	<5	<5	<5	<5	<5		
Hexazinone	<44	<23	<45	<1	<1	<1	<1	<1		
Iprodione	<10	<10	<10	<10	<10	<10	<10	<10		
Isofenphos	<2	<2	<2	<2	<2	<2	<2	<2		
Malathion	<2	<2	<2	<2	<2	<2	<2	<2		
Malathion, oxygen analog	<5	<5	<5	<5	<5	<5	<5	<5		
Metaxyl	<1	<1	<1	<1	<1	<1	<1	<1		
Methidathion	<2	<18.0	<2	<2	<2	<2	<2	<2		
Metolachlor	<1	<1	<1	<1	<3.0	<1	<1	<1		
Metribuzin	<4	<5.0	<4	<4	<4	<4	<4	<4		
Myclobutanil	<10	<1	<1	<1	<1	<1	<1	<1		
1-Naphthol	<10	<10	<10	<10	<10	<10	<10	<10		
Parathion-methyl	<2	<2	<2	<2	<2	<2	<2	<2		
Parathion-methyl, oxygen analog	<5	<5	<5	<5	<5	<5	<5	<5		
Pendimethalin	<1	<1	<1	<1	<1	<1	<1	<1		
Phorate	<5	<5	<5	<5	<5	<5	<5	<5		
Phorate, oxygen analog	<7	<7	<7	<7	<7	<7	<7	<7		
Prometon	<2	<2	<2	<2	<2	<2	<2	<2		
Prometryn	<2	<2	<2	<2	<2	<2	<2	<2		
cis-Permethrin	<5	<5	<5	<5	<5	<5	<5	<5		
trans-Permethrin	<5	<5	<5	<5	<5	<5	<5	<5		
Propyzamide	<2	<2	<2	<2	<2	<2	<2	<2		
Simazine	<2	<2	<2	<2	<2	<2	<2	<2		
Tebuthiuron	<3	<3	<3	<3	<3	<3	<3	<3		
Terbufos	<3	<3	<3	<3	<3	<3	<3	<3		
Terbufos-oxygen analog sulfone	<5	<5	<5	<5	<5	<5	<5	<5		
Terbutylazine	<1	<1	<1	<1	<1	<1	<1	<1		
Trifluralin	<1	<1	<1	<1	<1	<1	<1	<1		
$\alpha$ -HCH- <i>d6</i> surrogate, % recovery	50	61	67	60	52	58	133	85		
Diazinon- <i>d10</i> surrogate, % recovery	122	123	106	124	108	116	106	114		





**Table 20.** Concentrations of organohalogen compounds analyzed by gas chromatography/electron-capture negative ion mass spectrometry in lake-sediment samples collected in Rocky Mountain National Park and Glacier National Park in 2003.—Continued

[<, less than; E, estimated concentration; %, percent; concentrations reported in micrograms per kilogram of sediment (dry weight); shaded cells denote detectable concentrations; PCB, polychlorinated biphenyls; PBDE, polybrominated diphenyl ethers]

Compound	Rocky Mountain National Park			Glacier National Park				
	Black Lake 7/31/2003	Lake Haiyaha 8/13/2003	Ypsilon Lake 7/24/2003	Atsina Lake 9/11/2003	Lake Janet 9/13/2003	Mokowanis Lake 9/10/2003	Slide Lake 9/9/2003	Stoney Indian Lake 9/12/2003
<i>PCB congeners</i> —Continued								
PCB 174	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB 177	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB 180	0.37	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB 183	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB 187	0.29	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB 194	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB 206	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
<i>PBDE congeners</i>								
PBDE 47	<3.2	<3.2	<3.2	<3.2	<3.2	<3.2	<3.2	<3.2
PBDE 99	<3.2	<3.2	<3.2	<3.2	<3.2	<3.2	<3.2	<3.2
PBDE 100	<3.2	<3.2	<3.2	<3.2	<3.2	<3.2	<3.2	<3.2
PBDE 153	<3.2	<3.2	<3.2	<3.2	<3.2	<3.2	<3.2	<3.2
PBDE 154	<3.2	<3.2	<3.2	<3.2	<3.2	<3.2	<3.2	<3.2
$\alpha$ -HCH- <i>d6</i> surrogate, % recovery	55	56	55	61	58	62	65	70

was detected in only one snow sample (table 15) collected during the study, perhaps because the analytical detection limits were not low enough to detect these compounds.

To date, there have been few studies of pesticides and other organic compounds in lake or stream sediment in high-elevation parks in the Western United States against which to compare the results of this study. The most comparable data are from the sediment core collected at Mills Lake by the USGS in 1999 (P.C. Van Metre, unpub. data, 2000). The surface sediments (0–3 cm) from Mills Lake, which is about 2 km downstream from Black Lake, had a DDD concentration of 3.2  $\mu\text{g}/\text{kg}$  and a DDE concentration of 2.7  $\mu\text{g}/\text{kg}$ , which are very similar to the concentrations in Black Lake (2.2  $\mu\text{g}/\text{kg}$  DDD and 4.7  $\mu\text{g}/\text{kg}$  DDE; table 17) measured in this study. Stephens and Deacon (1997) analyzed streambed sediment and whole-body fish samples from the Colorado River near the western boundary of ROMO as part of the USGS National Water-Quality Assessment Program (NAWQA). None of the 33 organochlorine pesticides and PCBs analyzed for, which included DDT, DDE, and dacthal, were detected in the sediment; however, DDE was detected in a brown trout tissue sample collected at the same site. Sediment and fish tissue from North Saint Vrain Creek near the southeast boundary of ROMO were analyzed for organochlorine pesticides and PCBs as part of the South Platte NAWQA study (Tate and Heiny, 1996). Similar to the other NAWQA study, no organochlorine compounds were detected in sediment at this site and only DDE was detected in fish tissue. Heit and others (1984) determined levels of the PCB and PAHs in surface sediments (0–2 cm) from four lakes in ROMO including Lake Haiyaha, which was sampled as part of this study. Total PCB concentrations in the lakes ranged

from 21 to 540  $\mu\text{g}/\text{kg}$  (dry weight), and PAH concentrations (not measured in this study) ranged from 80 to 375  $\mu\text{g}/\text{kg}$ . The total PCB concentration at Lake Haiyaha was 160  $\mu\text{g}/\text{kg}$  compared to less than 15  $\mu\text{g}/\text{kg}$  measured as part of this study. This may reflect differences in the age of the lake sediments, which were nearly 20 years older in the Heit and others (1984) study than sediments analyzed as part of this study.

Sediment cores from lakes in six National Parks in the Western United States (including ROMO and GLAC) are being collected and analyzed for semivolatile organic compounds as part of WACAP (National Park Service, 2004). Preliminary results from Pear Lake in Sequoia National Park in California showed detectable levels of endosulfans and dieldrin in lake sediments that were deposited after 2000 (National Park Service, 2005). Rhea and others (2005) measured PAH concentrations in sediment from lakes in Grand Teton National Park in Wyoming. Sediment concentrations of total PAHs ranged from 5.7 to 471  $\mu\text{g}/\text{kg}$ , which were largely attributed to terrestrial and biogenic sources rather than anthropogenic sources. Several organochlorine compounds were measured in a sediment core from Wonder Lake in Denali National Park in Alaska (Cubala and others, 1995). Both DDE and DDT were detected only in surface sediments (less than 40 years old) at concentrations of 0.32 and 0.15  $\mu\text{g}/\text{kg}$ , respectively (Cubala and others, 1995). Other detected compounds in surface sediments from Wonder Lake included chlordane,  $\gamma$ -HCH (lindane), HCB, and several PCB congeners. In conclusion, this comparison indicates detections and concentrations of pesticides and other organic compounds observed in this study are similar to published results for similar studies.

## Summary

This report describes the occurrence and distribution of selected organochlorine compounds and current-use pesticides in snow and lake-sediment samples collected in Rocky Mountain National Park (ROMO) in Colorado and Glacier National Park (GLAC) in Montana during 2002–03. This study was conducted in cooperation with the National Park Service to provide baseline information on organic contaminants and to assess if current levels of these compounds pose a threat to aquatic organisms. This report includes data for snow samples that were collected at eight sites in ROMO and eight sites in GLAC during spring of 2002 and 2003 and data for surface sediments that were collected at 11 lakes in ROMO and 10 lakes in GLAC during summer months of 2002 and 2003. Samples were analyzed for organochlorine compounds by gas chromatography with electron-capture detection and current-use pesticides by gas chromatography with electron-impact mass spectrometry. A subset of samples was reanalyzed using a third instrumental technique (gas chromatography with electron-capture negative ion mass spectrometry) to verify detected concentrations in the initial analysis and to investigate the presence of additional compounds.

Because atmospheric deposition is the primary pathway by which contaminants enter remote high-elevation areas, snow samples were collected to determine which pesticides are currently reaching these ecosystems and at what rates. Snow was selected as a sample medium because snowfall provides most of the annual precipitation in high-elevation areas. Snow sampling has an advantage in that a single full-depth snowpack sample collected at maximum accumulation represents wet and dry deposition for the entire winter period. The snow sampling sites for this study were selected along elevation gradients on each side (east-west) of the Continental Divide. In ROMO, snow was collected at eight sites that spanned an elevation range of about 660 m, and in GLAC, snow was collected at eight sites that spanned an elevation range of about 700 m.

In snow samples, the pesticides most frequently detected were endosulfan, dacthal, and chlorothalonil, all of which are chlorinated pesticides that currently are registered for use in North America. The insecticide endosulfan (including the isomers endosulfan I, endosulfan II, and the degradate endosulfan sulfate) was detected in all of the snow samples analyzed by GC/ECNIMS in concentrations ranging from 0.07 to 1.18 ng/L. Dacthal, a herbicide, was detected in 50 percent of the samples analyzed by GC/EIMS in concentrations ranging from 0.33 to 2.2 ng/L. Chlorothalonil, a fungicide, was detected in all but two of the samples analyzed by GC/ECNIMS in concentrations ranging from 0.51 to 2.36 ng/L. Of the historical-use pesticides, dieldrin, HBC, and *trans*-nonachlor were detected in snow but only in one sample each. The concentrations of the detected pesticides in snow were not related to site elevation or location relative to the Continental Divide and were not notably different between forest and meadow sites. Concentrations were similar between the two parks with the exception of dacthal, which was slightly higher in ROMO compared to GLAC, which may reflect closer proximity of ROMO to agricultural areas.

Because the snow-sampling sites are remote, the most reasonable source of these pesticides is regional atmospheric transport from surrounding agricultural areas and subsequent wet and dry deposition to the snowpack. Estimated annual deposition rates of endosulfan, dacthal, and chlorothalonil were 0.7, 1.0, and 1.2  $\mu\text{g}/\text{m}^2$  in ROMO and 3.0, 1.2, and 1.0  $\mu\text{g}/\text{m}^2$  in GLAC, respectively. The larger deposition rates in GLAC primarily are a function of greater precipitation amounts in that park. Preliminary results indicate deposition during summer months was substantially greater than during winter, which emphasizes the importance of year-round monitoring to improve estimates of pesticide deposition to high-elevation ecosystems.

Surface sediments from lakes were collected to determine pesticide occurrence in sediments and if current levels of these compounds might pose a risk to aquatic organisms. Sediments were collected at 11 lakes in ROMO and 10 lakes in GLAC during summer months. Lakes selected for this study were high-elevation, oligotrophic lakes that supported trout populations. Lakes in ROMO ranged in elevation from 2,903 to 3,371 m and lakes in GLAC ranged from 1,463 to 1,926 m.

DDE and DDD were the most frequently detected compounds in lake-sediment samples. DDE and DDD are degradation products of DDT, which is a well-documented, persistent organochlorine insecticide that has been banned from use in the United States since 1972. In ROMO, all surface-sediment samples had low but detectable concentrations of DDE and one lake had detectable DDT. In GLAC, 9 of the 10 lakes had detectable concentrations of DDE in surface sediment. Although DDD and DDE were detected in most of the surface sediments, the concentrations were well below levels where harmful effects for benthic organisms are observed and probably pose little threat to aquatic organisms. Sediment concentrations of DDE and DDD were not related to lake elevation, surface area or depth, or lake location relative to the Continental Divide. The only notable spatial pattern was higher DDE and DDD concentrations in ROMO compared to GLAC, which may reflect closer proximity of ROMO to urban and agricultural areas. DDD and DDE concentrations in a sediment core from Mills Lake in ROMO showed increases with depth with the highest concentrations measured in sediments deposited during the 1970s, which correlates with its ban from usage in 1972. This result indicates that atmospheric deposition of DDT and possibly other banned organochlorine compounds to high-elevation parks has been in decline since their agricultural and industrial uses were discontinued.

Other commonly detected compounds in lake sediments included dacthal, endosulfan sulfate, and chlordane. Dacthal was detected in 50 percent of samples and endosulfan sulfate was detected in 75 percent of samples analyzed by GC/ECNIMS. Concentrations of both compounds were low, ranging from 0.11 to 0.26  $\mu\text{g}/\text{kg}$  for dacthal and 0.12 to 1.2  $\mu\text{g}/\text{kg}$  for endosulfan sulfate. Both dacthal and endosulfan were detected in nearly all the snow samples, confirming that some current-use pesticides entering aquatic ecosystems through atmospheric deposition are persistent enough to be accumulating in sediments in high-elevation lakes and potentially in aquatic biota as well.

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