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The Dynamics of Persistent Organic Pollutants in Air and in Selected Lakes of the Canadian Rocky Mountains

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Abstract

This thesis examines the concentrations of persistent organic pollutants (POPs) in air and in selected lakes of the Canadian Rocky Mountains. Water was sampled from seven lakes spanning an elevation of 1430 meters from the Interior Plains to the Western Range of the Canadian Rocky Mountains. Air samples were taken at four of these sites, encompassing an altitudinal gradient of 1205 meters. Air and water samples were used to determine net air-water gas exchange fluxes of six POPs at these four sites. This study revealed that air and water concentrations of several persistent organic pollutants did not change significantly with elevation. However, spring pulses of hexachlorocyclohexanes (HCHs) in the lakes were found to coincide with snowmelt, and concentrations of POPs were highest at Bow Lake during the year with the highest snow pack. It was observed that temperature differences with altitude had little impact on the magnitude and direction of air-water gas exchange, indicating net fluxes of POPs were most sensitive to fluctuations in relative air and water concentrations. Air-water gas exchange was compared with the total lake inventory and with estimated losses by outflow. In general, it was revealed that deposition by air-water gas exchanges was an important source of POPs with lower Henry's law constants, such as α and γ-HCH, and net volatilisation was an important loss for the compounds with higher Henry's law constants, (e.g. hexachlorobenzene (HCB) and dieldrin).

Résumé

La présente thèse examine la concentration de polluants organiques persistants (POPs) dans l'air et dans certains lacs des Montagnes Rocheuses du Canada. Des échantillons d'eau ont été ceuillis de huit lacs sur une marge d'élévation de 1430 mètres dans les Plaines Intérieures de la Chaines de l'Ouest des Roucheuses Canadiennes. Des échantillons d'air ont été pris de quatres de ces emplacements, ceux-ci sur une marge d'élévation de 1205 mètres. Les échantillons d'air et d'eau ont servis à determiner les flux nets d'échange de gaz air-eau pour six POPs à ces quatres sites. La présente étude a revelé que le changement de concentration de pluseiurs POPs dans l'air et l'eau n'etait pas significatif avec l'altitude à cause de concentrations variables dans l'air et l'eau. Par contre, des pulsations printaniers d'hexachlorocyclohexanes (HCHs) dans les lacs coincidant avec la fonte des neiges on été remarquées et une augmentation générale de concentrations de POPs a été observée au Lac Bow pour les années de pile de neige élevées. On a observé que la différence de température avec l'altitude avait peu d'impacte sur l'ampleur et la direction de l'échange de gaz air-eau. On a trouvé que les flux nets de POPs étaient plus sensibles aux fluctuations de concentrations relative dans l'air et l'eau. L'échange de gaz air-eau a été comparée avec l'inventaire total du lac et avec les pertes estimées par effluence. En général, on a trouvé que la déposition par échanges de gaz air-eau était une source importante de POPs plus soluble dans l'eau, tel que α et γ-HCH, et que la volatilisation était une perte importante pour les composés avec une constante de Loi d'Henry élevée, (e.g., comme le hexachlorobenzene (HCB) et le dieldrin).

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Glossary of Acronyms, Symbols, and Abbreviations

A	surface area between two distinct phases or compartments
a_1	slope of the Clausius-Clapeyron equation
a_2	first order rate constant
B	diffusivity ($m^2\ h^{-1}$)
B_{HV}	break through of POPs by high-volume air samples
C_a	chemical concentration in air ($pg\ m^{-3}$)
C_{equil}	chemical concentration in water when at equilibrium with air
C_w	dissolved concentration of a chemical in water ($pg\ L^{-1}$)
$C_{w\ actual}$	DOC corrected dissolved water concentrations ($pg\ L^{-1}$)
C_{wd}	measured water concentration in the dissolved phase ($pg\ L^{-1}$)
D_a	air diffusivity ($m^2\ d^{-1}$)
D_w	water diffusivity ($m^2\ d^{-1}$)
DBB	dibromobenzene
DCM	dichloromethane
DDD	dichlorodiphenyldichloroethane
DDE	dichlorodiphenyldichloroethylene
DDT	dichlorodiphenyltrichloroethane
DOC	dissolved organic carbon
ECD	electron capture detector
EXP	exponent
F	flux density ($ng\ m^{-2}\ d^{-1}$)
F_g	flux of organic compounds across the air-water interface
GC	gas chromatograph
H	Henry's law constant ($Pa\ m^3\ mol^{-1}$)
H(T)	temperature adjusted Henry's law constant ($Pa\ m^3\ mol^{-1}$)
H(Tr)	Henry's law constant of a chemical determined at a reference temperature
HCB	hexachlorobenzene
HCH	hexachlorocyclohexane
HP	Hewlett Packard
K_c	fraction of chemical bound to colloids in water
K_{oa}	octanol-air partition coefficient
K_{oc}	fraction of compound bound to organic carbon in water
K_{ol}	overall mass transfer coefficient ($m\ day^{-1}$)
K_{ow}	octanol-water partition coefficient
k_w	gas exchange coefficient ($m\ day^{-1}$)
L_A	Lake area (km^2)
masl	meters above sea level
M	molecular weight ($gram\ mol^{-1}$)
MDL	method detection limit ($pg\ L^{-1}$)
OC	organochlorine
O_D	daily loss of a chemical from outflow ($ng\ d^{-1}$)
o,p-DDT	ortho,para- dichlorodiphenyltrichloroethane
o,o-DDT	ortho,ortho- dichlorodiphenyltrichloroethane

Glossary of Acronyms, Symbols, and Abbreviations (continued)

P	partial pressure of a compound (atm)
P_{288}	partial pressure of a compound adjusted to 288 Kelvin
P_a	air pressure (pascal)
PAH	polycyclic aromatic hydrocarbon
PCB	polychlorinated biphenyl
PCDD	polychlorinated dibenzo-p-dioxin
PCDF	polychlorinated dibenzofuran
P_{meas}	measured partial pressure (atm)
POP	persistent organic pollutant
P_L	subcooled liquid vapour pressure (Pa)
PUF	polyurethane foam
PUF_{back}	concentration of POP on the back PUF plug (ng m^{-3})
PUF_{front}	concentration of POP on the front PUF plug (ng m^{-3})
R	universal gas constant (8.314 Pa m^3 mol^{-1} K^{-1})
R_a	air side resistance (day m^{-1})
R_w	water side resistance (day m^{-1})
S	total storage of a chemical in lake water (grams)
S_c	Schmidt number
S.D.	standard deviation
S.E.	standard error
T	temperature (Kelvin)
T_{meas}	measured temperature (Kelvin)
T_{res}	mean residence time of water in a lake (days)
t yr^{-1}	metric tonnes per year
TBB	tribromobenzene
TTBB	tetrabromobenzene
U_{10}	wind speed calculated at a ten meter height
V	viscosity (m^2 d^{-1})
Z_a	thickness of the stagnant air layer at the air-water interface
Z_w	thickness of the stagnant layer of water at the air-water interface
ΔC	change in chemical concentration
ΔH	enthalpy of phase-transition (K.J mol^{-1})
ΣPCB	sum of 130 PCB congeners
ρ	density (g L^{-1})

1.0 General Introduction

Persistent organic pollutants (POPs) are volatile and semi-volatile organic hydrocarbons that are resistant to rapid degradation in the environment. They encompass several groups of chemicals that include pesticides, polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), and polychlorinated dibenzo-p-dioxins and dibenzenofurans (PCDDs, PCDFs) (de March et al. 1998). Characteristics of POPs include their ability to persist, bioaccumulate in animal tissues and their toxicity to living organisms (Thomann 1989; de March et al. 1998). Most have the ability to travel long distances from source areas (Mackay et al. 1992, 1997; Wania and Mackay 1996). The adverse effects POPs have on human and environmental health have been well documented and have led to most POPs being restricted or banned in many developed countries (Cremlyn 1978; Hassall 1982). This report focuses on organochlorine (OC) insecticides and PCBs and the word POPs will be used to refer to these two classes of chemicals.

Some of these chemicals are now ubiquitous throughout the environment and have been found to reach the most remote regions of the earth (George and Frear 1966; Barrie 1986; Norstrom et al. 1988; Barrie et al. 1992; Wania and Mackay 1993; Bidleman et al. 1995). Detection of POPs in remote regions where emission sources are non-existent has lead many research scientists to examine how and why these pollutants are distributed globally. It has become evident that these chemicals were discharged in warmer regions, and then migrated to colder regions where they deposited onto terrestrial and aquatic surfaces (Rappe 1974; Goldberg 1975; Ottar 1981; Weschler 1981; Wania and Mackay 1992, 1993).

POPs travel around the globe by advection, with air and ocean currents. They can be found as vapours and in condensed phases (water, soil, and sediments) at ambient temperatures and pressures (Bidleman, 1988). Transfer of these chemicals from the atmosphere onto water surfaces can occur by wet deposition, dry particle deposition and partitioning from air to water across the air-water interface.

This thesis aims to identify distribution patterns of POPs in lakes spanning an altitude range in the Canadian Rocky Mountains. In the Rocky Mountains of Western Canada, Blais et al. (1998) found that deposition of POPs increased 10 to 100 fold between 770 and 3,100m altitude, with the increase of the less volatile compounds mostly due to the increased washout by precipitation at higher altitudes. The transport and subsequent deposition of POPs into lakes located in the Canadian Rocky Mountains may be dependent on where the chemicals are used, the chemical properties of the pollutants, climatic conditions, and the physical environment of the lakes and their surrounding catchment. The POPs emphasized in this report include the organochlorine insecticides; hexachlorocyclohexanes (HCHs), hexachlorobenzene (HCB), endosulfans, dieldrin, heptachlor epoxide, DDT and the polychlorinated biphenyls (PCBs).

1.1 Research Objectives

This project was commenced to determine the extent to which lakes in the Canadian Rocky Mountains have been contaminated with chlorinated pesticides and PCBs and to look at the effect that elevation has on contaminant distributions. Concentrations of POPs were examined in water at eight different sites, chosen to maximise a range of elevations. Air samples were also taken concurrently at four of those locations. Air and

water data were used together to determine the apparent magnitude and direction of the flux of POPs across the air-water interface. Seasonal changes in water concentrations of POPs were examined at all of the sites. At Bow Lake, trends in changing air and water concentrations of POPs were examined between the years 1997 through 2000. The locations and physical characteristics of the sites chosen are outlined in Figure 1.1 and Table 1.1 and 1.2. The generated data set was used to test the following hypotheses:

1. Air concentrations of POPs are foreseen to increase with increasing temperature. This was tested in chapter 2.0 by comparing seasonally averaged air concentrations with temperature.
2. Concentrations of compounds with lower K_{ow} will be greatest in spring during snowmelt, and concentrations in water will subsequently decrease as the snow pulse recedes. This hypothesis was tested in chapter 2.0 by examining how water concentrations of selected POPs changed from early spring to late summer.
3. We expect deposition from air-water gas exchange to be greatest in lakes at higher altitudes where air temperatures are cooler. As air and water masses warm with decreasing elevation, we expect air-water partitioning of POPs to progressively favour the air-side. This would result in a decrease in deposition and/or an increase in volatilization at lower altitudes. This hypothesis was tested in chapter 3.0 by calculating net air-water gas exchange at several sites spanning a 1205 meter range in elevation, and then comparing the magnitude and direction of the fluxes among all sites.
4. Net fluxes of POPs, from air-water gas exchange, will be evaluated to determine if deposition is greatest in early spring when lakes and air temperatures are still cool.

As air and water masses warm during the summer, we expect air-water partitioning of POPs to progressively favour the air side. This would result in a decrease in deposition and/or an increase in volatilization as the water and air masses warm during the summer. This hypothesis was tested in chapter 3.0 by calculating net air-water gas exchange, and then examining the magnitude and direction of the fluxes as they changed throughout the season.

5. The role of air-water gas exchange will be evaluated to determine how important it is to overall lake inventories. We predict that net deposition of POPs with lower Henry's law constants will be an important source of these chemicals to lakes. Likewise, we anticipate net volatilization for POPs with higher Henry's law constants will be an important loss from lakes. This hypothesis was tested in chapter 3.0 by calculating rates of air-water gas exchange in lakes during the sampling season, and comparing with the lakes' chemical inventory in water, and the estimated chemical losses by outflow.
6. We anticipate that concentrations of POPs in the lakes will increase with altitude as a result of cooler temperatures. We expect this pattern to be more pronounced for those compounds whose distribution is most affected by the temperature-dependent process of air-water gas exchange (see hypothesis 5). This hypothesis was tested in chapter 2.0 by comparing seasonally averaged lake water concentrations with altitude.

1.2 Chlorinated Insecticides

Typically, a pesticide is any substance used for the destruction or control of insects, birds, rodents, fungi, vegetation and any micro-biological agents (Hassall 1982;

Smith 1991). Pesticides can be divided into two main classes, contact or non-systemic pesticides and systemic pesticides (Cremlyn 1978). Contact pesticides do not penetrate plant tissue, while the systemic pesticides were designed to enter the vascular system of plants (Cremlyn 1978). The early pesticides were non-systemic and susceptible to the effects of weathering.

An insecticide is any substance used for the destruction or control of insects. Organochlorine insecticides are potent contact insecticides (Cremlyn 1978). They have high chemical stability because they are constructed largely from C-C, C-H and C-Cl bonds that tend to be chemically inactive under normal environmental conditions (Hassall 1982). These insecticides can be divided into three main families. The dichlorodiphenyltrichloroethane (DDT) family, which includes p,p-DDT, p,p-DDD and methoxychlor, is characterized by low water solubility and the potential for high bioaccumulation and biomagnification in birds, mammals and fish (Hassall 1982). Higher water solubility and the potential for wide distribution in the environment characterize the hexachlorocyclohexane (HCH) family, with γ-HCH being the only isomer with insecticidal properties. The chlorinated cyclodiene family includes aldrin, dieldrin, heptachlor, chlordane and endrin (Cremlyn 1978; Hassall 1982). These chemicals are characterized by high mammalian toxicity and some have a high potential for bioaccumulation in food webs.

The chlorinated insecticides originated with DDT and the HCHs. The insecticidal properties of DDT were discovered in 1939 during the Second World War. It was put on the market in 1943 and used by Allied soldiers in the tropics to control vector organisms responsible for diseases such as malaria and typhus. The insecticidal properties of γ-

HCH were discovered in 1943, and the organochlorine insecticide industry flourished after World War 2 as these compounds were praised for being effective, cheap and persistent (Cremlyn 1978).

1.2.1 DDTs

The synthesis of DDT was reported by Zeidler in 1874, (Cremlyn 1978). Sixty-five years later, in 1939, Dr. Paul Müller of the Swiss Geigy Company discovered the insecticidal properties of the p,p-DDT isomer (Cremlyn 1978). DDT is produced by condensation of chloral and chlorobenzene in the presence of an excess of concentrated sulphuric acid (Hartley and West, 1969). The crude product contains 80% p,p-DDT, 20% o,p-DDT and trace amounts of o,o-DDT. Pure p,p-DDT can be produced by recrystallization from ethanol at 108°C, but at an increased cost (Cremlyn 1978).

Commercial use of DDT began in 1943, after successful field tests in Switzerland against Colorado potato beetles (Cremlyn 1978). DDT soon became the most widely used insecticide in the world, largely because of its use as a controlling agent against malaria and typhus during World War 2, and its low toxicity to humans (Brooks 1974a).

The adverse environmental effects of DDT became well known to the world after Rachel Carson published "Silent Spring", in 1962. The ability of DDT to persist in the environment and to bioaccumulate and biomagnify in food webs became recognizable in raptors, bald eagles and peregrine falcons, when their populations sharply decreased because of eggshell thinning and reproductive failure. As a result, DDT use was restricted in the U.S. in 1973, in the U.K. in 1984 (Ayres and Hellier 1998), and banned in Canada in 1985 (de March et al. 1998). The use of DDT against malaria has saved

countless lives since it was first used in 1943. Approximately 2.5 billion people in over 90 countries are at risk of contracting malaria (WWF 1998), therefore DDT is still used in many of these developing countries (UNEP 1996).

1.2.2 HCHs

Hexachlorocyclohexane is the name used for the mixture of the eight isomers of the compound 1,2,3,4,5,6-hexachlorocyclohexane, denoted by the Greek letters ($\alpha,\beta,\gamma,\delta,\varepsilon,\eta,\theta$), with the α isomer existing in two enantiomeric forms (Willett et al. 1998). Michael Faraday created HCH in 1825 but its insecticidal properties were not recognized until 1942, in the laboratories of the Imperial Chemical Industries Ltd., England (Brooks 1974a). In 1943 it was discovered that the γ isomer was responsible for the insecticidal activity of technical HCH, (Brooks 1974a; Smith 1991). Technical HCH (or BHC) is composed of 60-70% α-HCH, 5-12% β-HCH, 10-12% γ-HCH, 6-10% δ-HCH and 3-4% ε-HCH (Kutz et al. 1991). Lindane, named after Van der Linden who discovered the isomer (Brooks 1974a), consists of more than 99% pure γ-HCH. HCH is produced by chlorinating benzene in the presence of U.V. radiation (Brooks 1974a). Subsequent treatment with methanol or acetic acid followed by fractional recrystallization will concentrate the γ-HCH isomer to 99.9% pure.

Technical HCH is very inexpensive to produce and until recently it was one of the most widely used insecticides in the world (Li et al. 1998). As a result, HCHs were found to be the most abundant organic chemicals in the arctic atmosphere and surface waters (Iwata et al. 1993; Bidleman et al. 1995). Unfortunately, 88% of technical HCH is useless as an insecticide and needlessly entered the environment where it has persisted

for years. Technical HCH was replaced by lindane in North America and Western Europe in the 1970s and then in China (1983), Russia (1990) and India after 1990 (Li et al. 1998; Willett et al. 1998). Lindane is currently used as an insecticide on fruits, vegetables, rice paddies, as a seed treatment and for the management of forestry products. On humans, it has been used for the treatment of lice and scabies (Willett et al. 1998).

Volder and Li (1995) estimated the cumulative global usage of technical HCH at 550 000 metric tonnes and 720 000 metric tonnes for lindane. More recent total global consumption of technical HCH has been estimated at 6.0 million metric tonnes (Li et al. 1998). The highest consumption of technical HCH occurred between 0-30° N latitude, while the highest consumption of γ-HCH occurred between 30°N and 60°N latitude (Volder and Li 1995). Canada and the United States banned the use of technical HCH in 1971 and 1978, respectively (Barrie et al. 1992; U.S. EPA 1978). The three biggest users of technical HCH were China, the Soviet Union and India. China banned technical HCH in 1983. The former Soviet Union banned technical HCH in 1990, after which India accounted for 98% of the worldwide use at approximately 28 400 t yr^{-1}. (Willett et al. 1998). On October 30th 1990, the government of India banned the use of technical HCH on most agricultural crops (Li et al. 1998) but continued to allow its use for public health protection and on certain food crops at a rate of 20 000 t yr^{-1}. (David 1992). Large quantities of HCHs are still found throughout the environment and are considered to be the most abundant organochlorine compounds in both air and water of arctic and sub-arctic regions (Bidleman et al. 1995).

1.2.3 Hexachlorocyclohexane (HCB)

First synthesized by Lorentz in 1893, HCB is a fully chlorinated aromatic hydrocarbon produced from ferric chloride and benzene (Ayres and Hellier 1998). It was first used in Canada in 1940 as a seed dressing for wheat, barley, oats and rye and to prevent fungal disease (Ayres and Hellier 1998). Its use in agriculture was discontinued in 1972 and 1976 due to concerns over adverse effects on the environment and its potential as a human carcinogen (CEPA 1994; Environment Canada 1997a). Current sources of HCB released into the Canadian environment includes; application of certain pesticides contaminated with HCB, release from incineration, leachates from hazardous waste landfills and emissions from certain industries (CEPA 1994). HCB has a low solubility in water (Table 1.3) and persists in the environment; therefore long-range transport plays a significant role as a continuing source of HCB throughout the globe. The primary mechanism for transport from the atmosphere to aquatic and terrestrial systems is wet deposition (Eisenreich and Strachan, 1992). Chemical and biological degradations are not important removal processes of HCB from water or sediments. Removal of HCB from water occurs primarily through outflow and by partitioning from water to air across the air-water interface (McConnell et al. 1996). HCB undergoes photolytic degradation in the troposphere, with a half-life of 80 days (Mill and Haag, 1986).

1.2.4 Chlorinated Cyclodiene Family

In 1956 Finkenbrink first described the insecticidal properties of endosulfan, and Hoechst first introduced the product later that year under the trade name Thiodan (Brooks

1974a). Endosulfan is a broad-spectrum, non-systemic contact insecticide, used mainly on fruit and vegetable crops as an acaricide (to kill mites) and in forestry (Brooks 1974a; NRCA 1975). Technical endosulfan is a mixture of two isomers, consisting of 7 parts α-endosulfan and 3 parts β-endosulfan. Once incorporated into soil the α-endosulfan isomer degrades quickly while the β-endosulfan isomer persists with a half-life of 2 years (Howard et al. 1991). The principal degradation product in the soil is endosulfan sulphate, which is also highly persistent and nearly as toxic as the parent compound. Half-lives of endosulfan in aquatic ecosystems can range from 5 weeks to five months (NRCC 1975). Endosulfan reacts with hydroxyl radicals in air with an atmospheric half-life of 2.5 to 25 hours (Atkinson 1987; Howard et al. 1991). Endosulfan is highly toxic to fish (Brooks 1974a) and becomes teratogenic when metabolized in mammals (Ayres and Hellier 1998). It is still approved for widespread use in North America (Rice et al. 1997; de March et al. 1998).

Aldrin and dieldrin are some of the most active contact insecticides (Cremlyn 1978). In Canada they were used to control soil insects, insects on agricultural crops, on forestry products, for industrial applications and dieldrin was used in sheep and cattle dips (Environment Canada 1997b). Dieldrin is formed by the epoxidation of aldrin (Hassall 1982) and when released into the environment aldrin is photochemically converted to dieldrin (Environment Canada 1997b). In air, aldrin has an atmospheric photo-oxidation half-life of between 55 minutes and 9.1 hours and dieldrin has a photo-oxidation half-life ranging from 4 to 40.5 hours (Howard et al. 1991; Environment Canada 1997b). In water, aldrin is converted to dieldrin by aquatic organisms (Environment Canada 1997b). The biodegradation half-life of aldrin in aquatic

ecosystems range between 3 weeks and 1.6 years and the half-life for dieldrin ranges from 175 days to 3 years (Howard et al. 1991). In response to environmental and human health concerns, most Canadian uses of aldrin and dieldrin were phased out in the 1970's (Environment Canada 1997b). In Canada, aldrin and dieldrin were only licensed for use in controlling termites from the mid 1970's until registration was discontinued in 1990 (PMRA 1996). These compounds are now banned in most developed countries because they are potent human carcinogens (Ayers and Hellier 1998) and they bioaccumulate and biomagnify in ecosystem food webs (Environment Canada 1997b).

The insecticidal properties of chlordane were reported in 1945 (Cremlyn 1978) and the product was introduced into the U.S. and Germany later that year (Hassall 1982). Chlordene is prepared from hexachlorocylopentadiene and cyclopentadiene by the Diels-Alder reaction (Cremlyn 1978). Subsequent addition of chlorine gives the highly active compound chlordane and heptachlor. The technical mixture of chlordane consists of 26 compounds (Ayres and Hellier 1998), however pure chlordane consists of the γ -(trans) isomer and the more toxic α -(cis) isomer (Hassall 1982). Experiments have found chlordane to be carcinogenic and to cause kidney and liver damage (Ayres and Hellier 1998). Its use was restricted in Canada in 1987 and it has been banned in most developed countries (Ayres and Hellier 1998).

Heptachlor is produced by the chlorination of chlordene by sulphuryl chloride in the presence of benzoyl peroxide catalyst (Cremlyn 1978). Heptachlor is converted to heptachlor epoxide, a more toxic compound, in living organisms (Cremlyn 1978). Chemically, heptachlor treated with chromium trioxide in sulphuric acid produces heptachlor epoxide (Brooks 1974a). Heptachlor was mainly used as a seed dressing and

as a soil fumigant (Brooks 1974a). Both heptachlor and heptachlor epoxide are known carcinogens (Brooks 1974b; Ayres and Hellier 1998).

All three organochlorine insecticide families are neurotoxic substances (Hassall 1982). The initial effect of DDT is on the peripheral nervous system while γ-HCH and the aldrin family attacks the central nervous system. Despite their adverse effects on environmental and human health, organochlorine insecticides have benefited civilization by increased food production and as a control for vector diseases. It has been suggested that "no other chemical made by man has saved so many lives as DDT", (Hassall 1982). Unfortunately the persistence of these toxic chemicals has lead to trace amounts in air and water being found throughout the entire world (Hassall 1982). Ambient exposure of these chemicals to animals has also caused adverse health effects such as impaired reproduction, weakened immunity and tumour promotion (de March et al. 1998).

1.3 Polychlorinated Biphenyls

Polychlorinated Biphenyls (PCBs) are non-polar, aromatic, chlorinated hydrocarbons. They have a biphenyl nucleus on which one to ten of the hydrogens have been substituted by chlorine (Erickson 1997). Commercial PCBs were synthesised by chlorination of biphenyl with chlorine gas, in which a mixture of all 209 possible congeners was produced (Erickson 1997). They were first synthesised in 1881 by Schmidt and Schulty (Waid 1986) but commercial production of PCBs didn't begin until 1929 under the trade name Aroclor (Monsanto, U.S.) as a response for the electrical industry's need for a safer insulator. The thermal stability, resistance to degradation and low dielectric properties of PCBs made them desirable for uses as hydraulic fluids, as a

flame retardant in lubricating oils and as a cooling and insulating fluid for industrial transformers and capacitors (CCREM 1986). PCBs were also used as plasticizers in sealants, caulkings, synthetic resins, rubbers, paints, waxes and asphalts; and as surface coatings for carbonless copy paper (CCREM 1986). The manufacture, processing, distribution and uses of PCBs were banned as of January 1st 1978, by the U.S congress (Erickson 1997). Uses were banned throughout the rest of the world soon after (CCREM 1986).

Durfee et al. (1976) estimated that 1.3 billion pounds of PCBs had been produced world wide (93% produced by Monsanto), while another estimate put total production through 1980 at 2.4 billion pounds (unpublished, Bletchly 1983). Large amounts of PCBs have entered the environment from direct dumping, open burning, incomplete incineration, vaporisation from paints, leakage into sewers and streams and currently they still leak out of old transformers and fluorescent lights (CCREM 1986).

PCBs are semi-volatile, highly insoluble in water and undergo long-range atmospheric transport in the environment. The lower chlorinated PCBs are more volatile and generally capable of longer-range transport in the environment. They are also more easily excreted by fish and mammals. The higher chlorinated PCBs are less water-soluble. Therefore they bind more readily to soil and particulate matter and accumulate in lipids to a greater extent (Waid 1986; Erickson 1997). Water solubility ranges from 6 ppm for monochlorobiphenyls to 0.007 ppm for octachlorobiphenyls (Waid 1986). The persistence of PCBs coupled with their ability to bioaccumulate in food webs has caused great environmental damage. Through extensive *in vitro* and *in vivo* animal studies and human studies from accidental exposures, PCBs have been linked to decreased

reproduction in predatory birds, immunotoxicity, hepatotoxicity, endocrine effects, neurotoxicity, thymic atrophy, dermal toxicity, carcinogenicity, enzyme induction and liver damage in higher animals (Erickson 1997).

1.4 Transport of Persistent Organic Pollutants in the Environment

POPs are ubiquitous throughout the environment and are found in the most remote regions of the world (George and Frear 1966; Barrie 1986). They are capable of travelling around the globe by air and ocean currents (Bailey et al. 2000). Entry into the atmosphere can occur directly during applications, from evaporation shortly after application or they can volatilize from soil, water and vegetation during periods of higher temperatures months or years later (Hoff et al. 1998; Wania and Mackay 1993; Wania et al. 1998). Once in the environment, the semi-volatile nature of POPs enables them to evaporate and deposit among air, water and soil compartments at ambient temperatures and pressures (Bidleman 1988; Wania and Mackay 1996).

In general, POPs evaporate from terrestrial and water surfaces in warm source regions and then, through long range transport, deposit from the atmosphere onto terrestrial and water surfaces in colder regions. Wania and Mackay (1993, 1995, and 1996) have described how this process occurs by fugacity-based models. The condensation of airborne chemicals onto terrestrial and aquatic surfaces, which is accelerated in colder regions of the world, is known as the "cold-condensation" effect (Ottar 1981; Wania and Mackay 1993). There are three main factors that cause POPs to condense and accumulate in cold environments. The first is that cool temperatures favour greater adsorption of POPs onto atmospheric particulate matter, which then deposit onto

the earth's surface. Secondly, natural decomposition rates slow down in cold areas. Thirdly, cold temperatures decrease evaporation rates (Wania and Mackay 1993, 1996).

The theory of "global distillation" suggests that some of the more volatile POPs are evaporating from warmer source regions and depositing in polar environments where cold condensation is favoured (Goldberg 1975; Wania and Mackay 1993, 1996). The theory of "global fractionation" suggests that during global distillation, compounds become separated with latitude because of differences in their physical and chemical properties (Fig. 1.2) (Wania and Mackay 1996). As a result, the less volatile compounds tend to deposit and accumulate closer to their source, while the more volatile POPs undergo long-range atmospheric transport before temperature dependent partitioning onto terrestrial and aquatic surfaces (Fig. 1.2) (Gregor and Gummer 1989; Mackay and Wania 1995; Donald et al. 1999; Grimalt et al. 2001). The "grasshopper effect" (Wania and Mackay 1996), describes the migration process of POPs during global distillation. According to this theory, POPs migrate in a series of short jumps whereby the compounds migrate, rest and migrate again in tune with seasonal temperature changes. The more volatile POPs will migrate further and faster than the less volatile ones. Blais et al. (1998) observed an increase in the more volatile PCB congeners in snow pack at higher altitudes relative to the less volatile PCB congeners, in the Canadian Rocky Mountains.

Two important characteristics of chemicals that determine if they undergo global transport and distillation, are the vapour pressure of the subcooled liquid (P_L) and the octanol-air partition coefficient K_{oa} (Bidleman 1988; Weiss 2000). Vapour pressure describes the tendency for liquids to evaporate and for solids to sublime. Wania and

Mackay (1996) have suggested that POPs with a subcooled liquid vapour pressure above 1 Pascal (Pa) will show little tendency to condense in the global environment, while POPs with a P_L less than 0.0001 Pa do not evaporate and tend to deposit and accumulate locally. Condensation in this context is defined as the temperature at which 50% of the chemical is found in the vapour form and 50% is bound to aerosols. The semi-volatile organic compounds that are able to undergo long range transport and global fractionation have a P_L between 1 and 0.0001 Pa. POPs with a P_L between 1 and 0.01 condense at around -30°C, with the potential to accumulate in polar and alpine environments. Compounds with a P_L between 0.01 and 0.0001 Pa condense at temperatures above 0°C and may accumulate in mid-latitudes (Fig. 1.2) (Wania and Mackay 1996). The octanol-air partition coefficient (K_{oa}) is the concentration ratio of a chemical in octanol and air at equilibrium (Wania and Mackay 1996), and accounts for the ability of terrestrial surfaces to retain a compound (Weiss 2000). Substances that have a high hydrophobicity, K_{oa} between 10^8-10^{10}, will readily bind to soil, vegetation and aquatic sediments and will not be transported far from their source. Compounds with a low K_{oa}, between 10^6-10^8 will be very mobile in the environment (Wania and Mackay 1996). The POPs examined in this report have chemical characteristics that allow them to undergo long range transport and global distillation (Table 1.3).

Condensation and accumulation of POPs has occurred in arctic and sub-arctic lakes and oceans (Falconer et al. 1995; Jantunen and Bidleman 1998; Mackay and Wania 1995) as well as in high altitude snow packs in mid-latitude mountain ranges (Blais et al. 1998). These compounds are toxic and concerns have been raised about their effects on environmental and human health. Accumulation of certain POPs in arctic and antarctic

regions has been well documented, but few studies have looked at their distribution and fate in cold mountain environments. The accumulation of POPs in cold mountain lakes will be examined in this thesis with the idea that high altitude lakes may contain similar levels of persistent organic pollutants as arctic and sub-arctic water bodies.

1.5 The movement of chemicals through air and water

Molecular diffusion is the movement of chemicals from a region of higher concentration to a region of lower concentration due to thermal motion (random constant movements). The speed of the movement is dependent primarily on the size of the molecules and the temperature of the environment, with diffusion increasing in velocity at higher temperatures and for smaller molecules (Hemond and Fechner-Levy 2000). The mass transfer coefficient of a chemical is the net diffusion velocity with units of velocity (cm s^{-1}), (Mackay 1991). Diffusivity is the product of velocity across a distance and is affected by the weight of the molecule. At environmental temperatures, the diffusivity for most chemicals in air is approximately 0.2 cm^2 sec^{-1} and in water it is about 10^{-5} cm^2 sec^{-1} (Hemond and Fechner-Levy 2000).

1.5.1 Schmidt Number (S_c)

A Schmidt number (S_c) is derived from the ratio of the kinematic viscosity (m^2 d^{-1}) of a compound to the molecular diffusion coefficient (m^2 d^{-1}), where m is meter and d is day. Kinematic viscosity is the ratio of the dynamic viscosity of a fluid to the density of the fluid. Diffusivity raised to the power of 0.5 (in water) or 0.67 (in air), gives the

empirical dimensionless form of molecular diffusivity, the Schmidt number. It can be calculated with the equation (Mackay 1991):

$$S_c = V/\rho B \qquad (1.1)$$

Where V is viscosity, ρ is density and B is diffusivity ($m^2\ d^{-1}$). The Schmidt number is used when determining air-side resistance with air diffusivities and water-side resistance with water diffusivities, according to the two-film resistance model.

1.5.2 The Two-Film Resistance Model

The two-film resistance model (Whiteman 1923, Schwarzenbach et al. 1993) was used to determine the transport of POPs across the air-water interface of selected lakes. This model envisions a stagnant layer of air about 1mm in thickness and a stagnant layer of water approximately 0.1mm in thickness, at the air-water interface. Concentrations of chemicals in the boundary layers of air and water are different from their bulk volumes because they are slowly mixed by diffusion. It is assumed that bulk air and water masses are uniformly mixed by eddy currents (Schwarzenbach et al. 1993; Hemond and Fechner-Levy 2000). Turbulent air consists of the troposphere down to 1mm above the water surface and turbulent water consists of the entire body of water up to 0.1mm below the air surface. Molecular diffusivities in both air and water are critical traits needed to describe air-water mass transfer, since transfer occurs only by molecular diffusion, and the concentration gradient between the two phases drives the direction of the chemical transfer (Whitman 1923; Hemond and Fechner-Levy 2000). The overall rate of chemical transfer is controlled by the rate of transport through the two boundary layers (Hemond and Fechner-Levy 2000), therefore the stagnant layer with the highest resistance to mass

transfer determines the total resistance to mass transfer between the bulk water and air. When both phases are at equilibrium, the Henry's law constant of a chemical governs its concentration in water and air at the air-water interface (Schwarzenbach et al. 1993).

The Henry's law constant (H) of a chemical is the ratio of vapour pressure to water solubility (Mackay 1991). Henry's law constants for organic compounds are calculated experimentally by measuring air and water concentrations at equilibrium, in a closed system using pure water and have units in Pa m^3 mol^{-1} (Mackay 1991). Because this value changes with temperature, calculation of air-water exchange fluxes requires Henry's law constants to be adjusted to the temperature of the lake at the time of sampling. Air and water concentrations of POPs and temperatures are the most significant variables that determine the magnitude and flux of air-water gas exchange. However, wind velocity is also important to the overall flux of a chemical across the air-water interface. As wind velocity increases, the wind shear stress at the air-water interface decreases the thickness of the stagnant air layer and the stagnant water layer. This decreases the phase transfer resistance of chemicals between the two layers and as a consequence, the rate of diffusion between water and air increases (Schwarzenbach et al. 1993). Therefore, net fluxes can vary widely from hour to hour with changes in wind speed. Surface waves and turbulent surface waters can also influence the air-water gas exchange of POPs (Livingston and Imboden 1993), with high wind speeds and storms being important contributors to the overall flux of POPs into lakes, rivers and oceans (McConnell et al. 1996).

In general, the flux of a chemical from one phase to another is given by the equation (Mackay 1991):

$$F = k_{ol} * A * \Delta C \quad (1.2)$$

where F is the flux density (ng m^{-2} d^{-1}), k_{ol} is the overall mass transfer coefficient (m d^{-1}), A is surface area at the boundary layer interface (m^2) and ΔC is the change in chemical concentration (ng m^{-3}).

The fluxes of chemicals across the air-water interface can be directly related to concentrations and Henry's law constants. The concentration of a dissolved gas or vapour in surface water at equilibrium with the atmosphere is defined by the equation (Hemond and Fechner-Levy 2000):

$$C_{equil} = C_a \, RT/H \quad (1.3)$$

Where C_{equil} is the chemical concentration in water at equilibrium with air, C_a is the chemical concentration in the vapour phase (ng m^{-3}), R is the universal gas constant (8.314 Pa m^3 mol^{-1} K^{-1}), T is the absolute temperature (Kelvin), and H is the chemical's Henry's law constant (Pa m^3 mol^{-1}). If the concentration of the chemical in water is higher than C_{equil}, the chemical will volatilize from water.

1.5.3 Water-side control

If the Henry's law constant of a chemical is much greater than 0.01, resistance to gas exchange in the stagnant air layer can be neglected. The two-film resistance model then describes the flux of a chemical by (Hemond and Fechner-Levy 2000):

$$F = -D_w(C_w - C_a \, RT/H)/Z_w \quad (1.4)$$

where F is the flux density (ng m^{-2} d^{-1}) and D_w is the molecular diffusion coefficient for that chemical in water (m^2 d^{-1}). C_w is the chemical concentration in water (pg m^{-3}) corrected for dissolved organic carbon (DOC). Z_w is the approximated thickness of the

boundary layer of water determined by wind speed, about 0.1 mm in thickness. If the atmospheric concentration of a chemical is zero, this equation simplifies to:

$$F = (-D_w/Z_w)\, C_w = -k_w\, C_w \qquad (1.5)$$

where k_w is the gas exchange coefficient.

1.5.4 Air-side Control

If the Henry's law constant of a chemical is much less than 0.01, then molecular diffusion through the stagnant boundary layer of air becomes the most significant barrier to air-water gas exchange. Resistance due to the stagnant water film becomes insignificant. The flux through the stagnant air film is given by (Hemond and Fechner-Levy 2000):

$$F = -(D_a/Z_a).\ (C_w{*}RT/H - C_a) \qquad (1.6)$$

where D_a is the molecular diffusion coefficient for the chemical in air ($m^2\ d^{-1}$), Z_a is the approximated thickness of the stagnant air layer, about 1.0 mm. If the Henry's law constant of a chemical is on the order of 0.01, then both resistances contribute to limiting air-water gas exchange. Adding both resistances gives the equation (Hemond and Fechner-Levy 2000):

$$F = -[1/(Z_w/D_w) + Z_a/(D_a{*}RT/H)]\ [\ C_w - C_a\, RT/H] \qquad (1.7)$$

The overall flux (F) of organic compounds across the air-water interface was calculated using the following equation:

$$F = K_{ol}\,[(C_w - (C_a\, RT/H)] \qquad (1.8)$$

where K_{ol} is the overall mass transfer coefficient ($m\ d^{-1}$). The Henry's law constant values were adjusted for water temperature at the time of sampling using values

calculated by Tateya et al. (1988), Kucklick et al. (1991), Ten Hulscher et al. (1992) and Rice et al. (1997). DOC corrected water concentrations were determined using the following equations:

$$C_{w\,actual} = C_{wd} / (1 + (K_c * DOC)) \quad (1.9)$$

Where DOC is dissolved organic carbon in (mg L^{-1}) and C_{wd} is the measured water concentration in the dissolved phase (pg L^{-1}). K_c is the fraction of chemical bound to colloids in the water column and is calculated with the equation:

$$K_c = 0.2 * K_{oc} \quad (1.10)$$

Where K_{oc} represents the fraction of compound bound to organic carbon as follows (Landrum et al. 1984; Jeremiasson et al. 1999):

$$K_{oc} = 0.41 * K_{ow} \quad (1.11)$$

K_{ow} is the octanol:water partition coefficient. K_{ol} is determined on the basis of air-side resistance (R_a) and water-side resistance (R_w) as follows:

$$1/K_{ol} = R_a + R_w \quad (1.12)$$

Air-side resistance was calculated with air diffusivities (Schwarzenbach et al. 1993) as follows:

$$R_a = 1/[(D_a/D_a O_2)^{0.67} H/RT (0.2 U_{10} + 0.3) 864] \quad (1.13)$$

where D_a is an air diffusivity ($cm^2\ sec^{-1}$), and U_{10} is wind speed at a 10m height ($m\text{-}sec^{-1}$) and 1/864 converts sec cm^{-1} to d m^{-1}. Wind speeds were measured with an anemometer and converted to U_{10} with the conversion of Schwarzenbach et al. (1993). Water-side resistance under stagnant conditions was calculated with water diffusivities and U_{10} as follows:

$$R_w = 1/[(D_w/D_w O_2)^{0.5} (4x10^{-5} U_{10}^2 + 4x10^{-4}) 864] \quad (1.14)$$

Values for $D_a H_2O$ and $D_w O_2$ are 0.26 $cm^2 s^{-1}$ and $2.1x10^{-5}$ $cm^2 s^{-1}$, respectively. All other diffusivities were calculated using the compounds' molecular weights (M) with the following equation (Schwarzenbach et al. 1993):

$$D_x^{unknown} / D_x^{known} = (M_{known} / M_{unknown})^{0.5} \quad (1.15)$$

1.6 The Canadian Rocky Mountains

The Canadian Rocky Mountains are characterized by a vast, pristine wilderness located in rugged terrain, with great climatic variability. As the crow flies, the Canadian Rockies are 1450km in length spanning from the Liard River in Northern British Columbia to the international boundary in the south, and they run 150km in width from the Rocky Mountain Trench in the west to the Front Range in the east (Encyclopaedia Britannica 1992; Gadd 1995). They encompass an area of 180 000 km^2 and elevation ranges from 305 meters above sea level (masl), confluence of the Liard and Toad rivers (B.C), to 3954 masl, Mt. Robson (AB) (Encyclopaedia Britannica 1992). Running from north to south, the Rocky Mountain Range is geographically divided into three parts. The Northern Rockies extends from the Peace River in the south to the Liard River in the North and the highest point is Mt. Smythe, 2990 meters in elevation. The length of the central Rockies span from Crows Nest Pass in the south to the Peace River in the North and the highest point is Mt. Robson (3954 meters). The Southern Rocky Mountain Range spans from Marias Pass at the southern end of Glacier National Park to Crowsnest Pass in the North and the highest point is Mt. Cleveland (3190 meters) (Gadd 1995).

The Central Rockies, our region of interest, is further divided into five east-west physiographic divisions from Calgary (AB) in the east to Golden (B.C) in the west. The foothills begin about 25km west of Calgary and separate the interior plains from the

Rocky Mountains. They are visible as small rolling hills created by folds and faults. Continuing westward the foothills abruptly give way to the Front Range, with an average peak height of 2500 meters and tree line at 2300 meters (Gadd 1995). The Main Ranges start midway between Banff and Lake Louise and they are considered the backbone of the Rockies, with the average peak height at 3000 meters. The Main Ranges receive significantly more precipitation than the Front Range because of the higher elevations. Following the Trans-Canada highway, the Eastern Main Range begins around Castle Mountain and continues through to Field (B.C). The Continental Divide is located just west of Lake Louise, with the summit pass at1630 meters. The Western Main Range begins just west of Field and continues to Golden (B.C). The Western Range begins west of Golden and ends at the Southern Rocky Mountain Trench. This zone is the smallest, only 100km long and 20km across, it is found between Radium Hot Springs and Golden (Gadd 1995).

1.6.1 Climate and Weather in the Canadian Rockies

The mountains are notorious for great climatic variety and seasons can vary greatly from year to year. Mountains contain their own microclimates, with great differences between the north side and the south side (Schmidt 1986). The south side of a mountain receives sunlight throughout most of the day, while the north side remains largely in the shade. As a consequence, the south side of a mountain is warmer and drier compared to its north side (Schmidt 1986; Barry 1992). The weather in the mountains also varies drastically from moment to moment and can be quite different between adjacent mountains (personal observations).

Under the Koeppen classification system, climatoligists have classified this region "Dfc": "a cold, snowy forest climate with no distinct dry season and short, cool summers." It is also classified as a "continental climate", characterized by high temperature variability (Gadd 1995). In an average year, temperatures in Banff range from -40°C in January to +30°C in July. The high latitude contributes to the temperature variability because of drastic changes in daylight hours between seasons. At Lake Louise there are only 8 hours of sunlight each day in December and January but 16.6 hours of sunlight in June and July (Gadd 1995).

The high latitude is one reason for the cool temperatures in this region because the low-angle of sunlight has less irradiant energy than high angle sunlight further south. The average mean annual temperature for all public weather stations on valley floors is 2.6°C, with an average mean annual precipitation of 571mm (Gadd 1995). The western slopes are generally wetter and warmer, especially in the winter, compared to the cooler and drier eastern slopes. The prevailing winds are from the south west, however most of the pacific moisture is lost to the Coastal Mountains and Columbia Mountains, leaving less moisture to fall on the Rockies. This leaves the Front Range in a "rain shadow". Winds tend to come from the east in early summer and during mid-winter cold snaps. When the prairie air is pushed into the mountains, atmospheric moisture condenses into clouds and rain will fall in the foothills and Front Range, called "up-slope weather" (Gadd 1995).

When a dry air mass is forced up the mountain, temperatures can drop up to 1.0°C for every 100-meter gain in elevation (Barry 1992; Whiteman 2000). Generally, the air temperature drops 0.6 to 0.7°C for every 100-meter gain in elevation, due to thinning of

the atmosphere (Barry 1992; Whiteman 2000). Differences occur because some of the cooling in moist air is offset by latent heat that is released when vapour condenses into cloud droplets (Whiteman 2000). The production of clouds and precipitation that occurs from cooling and condensation when air rises over mountains is called orographic lifting (Barry 1992; Whiteman 2000). Typically, mountains get colder, wetter and windier with increasing elevation (Schmidt 1986; Barry 1992). That is why the subalpine forests on the western slope receive the most snow and the montane valleys in the Eastern Front Range receive the least snow. The snowiest region in the Rockies is along the continental divide between Lake Louise and Jasper. Snow lies deepest just below tree line and it reaches its greatest thickness in late March or early April (Gadd 1995).

1.7 Study Sites

This research spans eight sites that extend the width of the Canadian Rockies (Table 1.1; Figure 1.1). Going from east to west: Dixon Dam (946 masl) is located in the interior plains, just west of the town Innisfail (AB) (Table 1.1) and has a dry "continental" climate (Table 1.2). The lake is man made and fed by the Saskatchewan River. It is surrounded by agricultural land and there is a public beach on the south side of the lake. The surrounding bedrock consists of sandstone, siltstone, mudstone, thin limestone, coal and tuff beds (Crosby 1990). Lower Kananaskis Lake (1667 masl) is located in the Front Range of the Rockies in Peter Lougheed Provincial Park and has a cool moist climate because of altitude (Table 1.2). Kananaskis Lake is man made and contains campgrounds on the east shore. The bedrock geology consists of sandstone, siltstone, shale and carbonates (Crosby 1990). Vermilion Lake (1380 masl) is located in

the Front Range in Banff National Park, just outside the town of Banff (AB) (Table 1.1). The lake is very shallow and eutrophic (Table 1.2). The surrounding bedrock consists mostly of shale and dolomite (Gadd 1995). Rock Isle (2200 masl) is found in the Front Range in Mt. Assinaboine Provincial Park (BC) (Table 1.1) and is located just above a ski resort, Sunshine Village (AB). It is the highest and coldest of the sites and receives the most snow (Table 1.2). The bottom of the lake is mainly bedrock, made up of limestone and dolomite (Gadd 1995). Bow Lake (1975 masl) is located on the continental divide in Banff National Park, on the ice-fields parkway about 30km north of Lake Louise (Table 1.1). It is a glacially fed lake with a cold climate and receives high rates of precipitation (Table 1.2). The bedrock in this region consists of dolomite, limestone, Cambrian carbonates and shales (Smith 1978; Gadd 1995). Two sites were sampled at Bow Lake, the outflow of the lake and a glacial stream that contributes 73% of the total inflow to the lake (Blais et al. 2001a). Wapta Lake (1590 masl) is located on the continental divide just west of the pass summit, in Yoho National Park (BC) (Figure 1). The littoral zone of the lakes consists of gravel, cobble and pebbles (Beane 1989) originating from limestone and dolomite bedrock (Table 1.2). Donald (770 masl) is located 20km west of Golden in the Western Range of the Rockies (Fig. 1). The water is very turbid with high DOC content and shale bedrock (Gadd 1995). This site is a part of the Columbia River, immediately before it enters Kinbasket Lake. Collectively, these lakes span a wide range of elevations over a short distance. Therefore, these sites are advantageous for studying the impact of altitude and related climatic conditions on the distribution of POPs in the environment.

Table 1.1 Altitude, latitude, longitude, and location of the sampling sites.

Study Site	Altitude (masl)	Latitude	Longitude	Location in the Canadian Rockies
Rock Isle Lake	2200	51° 04'N	115° 47'W	Eastern Main Range
Bow Outflow	1975	51° 40'N	116° 25'W	Continental Divide
Bow Glacial Stream	1975	51° 40'N	116° 25'W	Continental Divide
Lower Kananaskis Lake	1667	50° 40'N	115°10'W	Front Range
Wapta Lake	1590	51° 26'N	116° 25'W	Continental Divide
Vermilion Lake	1380	51° 10'N	115° 34'W	Front Range
Dixon Dam Lake	946	52° 03'N	114°19'W	Interior Plains
Donald Station	770	51° 30'N	117° 10'W	Western Range

Table 1.2 Lake area, lake volume, mean residence time, mean annual temperature and mean annual precipitation of the study sites. Precipitation is total mm yr^{-1}, and the number in brackets is the amount of snowfall in mm yr^{-1}.

Study Site	Altitude (masl)	Lake Area (m^2)	Lake Volume (m^3)	Mean Residence Time	Mean Annual Temp.	Mean annual precipitation (mm yr^{-1} water eq.)
Rock Isle Lake[5]	2200	$4.9x10^4$	$2.09x10^5$	N/A	-2.4 °C	1000 (800)
Bow Lake[3,4]	1975	$2.8x10^6$	$5.6x10^7$	205 days	-1.8 °C	825 (550)
L. Kananaskis[1,8]	1667	$5.25x10^6$	$7.0x10^7$	113 days	1.3°C	622 (305)
Wapta Lake [2,3]	1590	$2.4x10^5$	$1.02x10^6$	1.3 days	-0.4°C	602 (329)
Vermilion [6,7]	1380	$1.5x10^5$	$1.99x10^5$	N/A	2.9°C	468 (244)
Dixon Dam[1,8]	946	$1.76x10^7$	$2.05x10^8$	73 days	2.3°C	467 (125)
Donald Station[1,7]	770	N/A	N/A	N/A	4.6°C	491 (184)

Data are from ....
1 Environment Canada Weather Services
2 Beane, M. (1989)
3 Lafreniere, M. (pers. comm.)
4 Campbell, L. (1995)
5 Harper, R. Mountain Operations (pers. comm.)
6 Pacas, C. Parks Canada (pers. comm.)
7 Gadd, B. (1995)
8 Crosby, J. (1990)

Table 1.3 Physical and chemical properties of selected persistent organic pollutants. Data are from Mackay et al. (1992; 1997), Rice et al. (1997). Henry's law constants and vapour pressures are calculated for 25°C.

Chemical Compound	Water Solubility ($g\ m^{-3}$) 25°C	Henry's Law Constant ($P_a\ m^3\ mol^{-1}$), at 25°C	Subcooled pressure (P_L, P_a)	Sorption coefficient Log K_{oc}	Octanol-water coefficient Log K_{ow}
α-HCH	1.0	0.87	0.1	3.8	3.8
γ-HCH	7.3	0.15	0.027	3.0	3.7
α-endosulfan	0.5	6.6	0.008	3.4	3.6
β-endosulfan	0.45	0.88	0.39	3.5	3.8
HCB	0.005	130	0.25	5.2	5.5
Aldrin	0.02	91	0.03	2.6	3.0
Dieldrin	0.17	1.1	0.016	4.1	5.2
p,p-DDT	0.005	2.4	1.35×10^{-4}	5.0	6.2
Heptachlor	0.056	350	0.27	4.4	5.3
Heptachlor epoxide	0.35	N/A	N/A	4.0	5.0
α-chlordane	0.056	0.34	2.65×10^{-3}	5.5	6.0
β-chlordane	0.056	0.26	3.15×10^{-3}	5.5	6.0

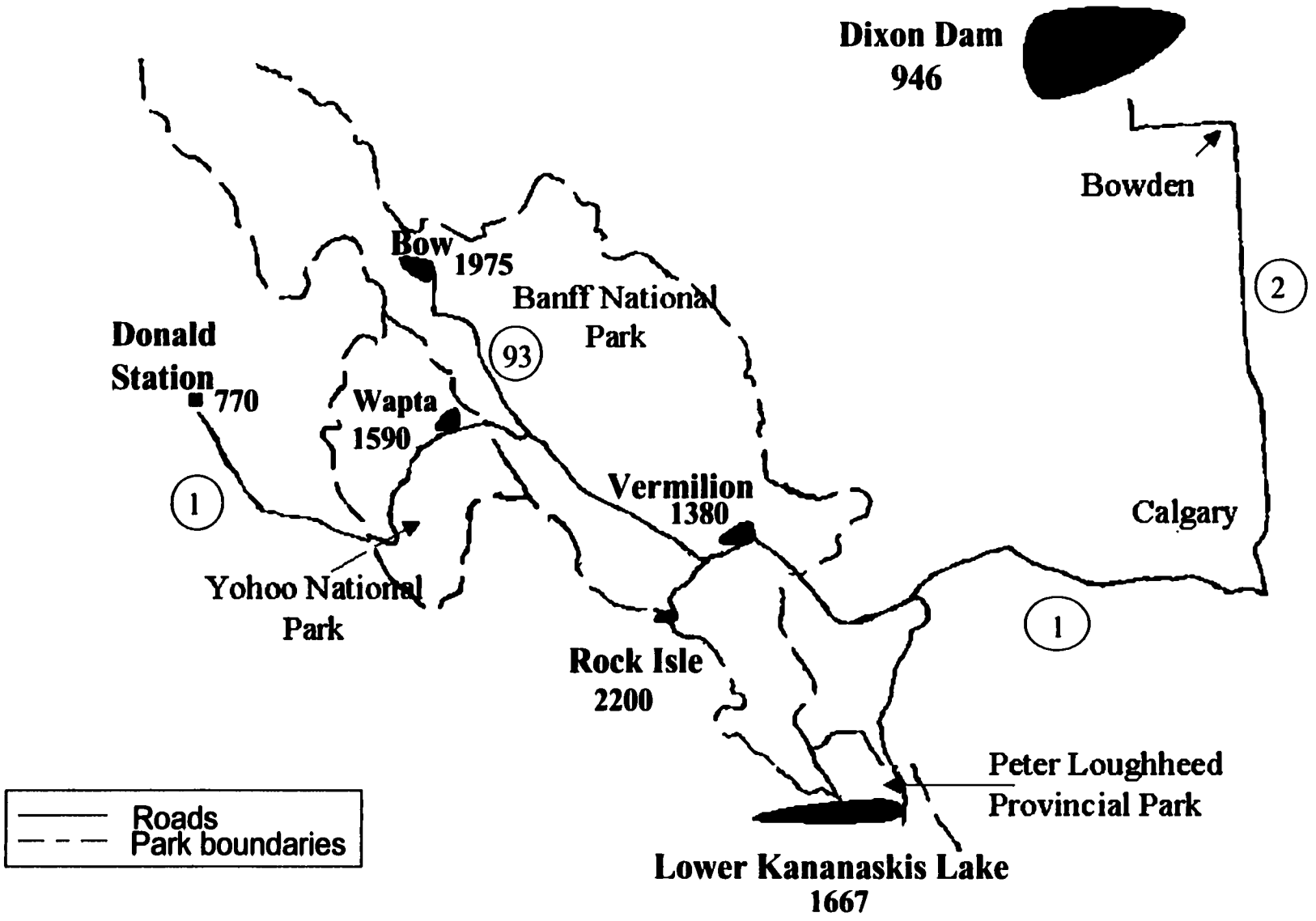

Figure 1.1 Map of sample sites used for the analysis of organochlorines and polychlorinated biphenyls in lake water. The solid lines represent roads and the dashed lines represent park boundaries. Site names are in bold font and their corresponding elevations are in meters above sea level (masl).

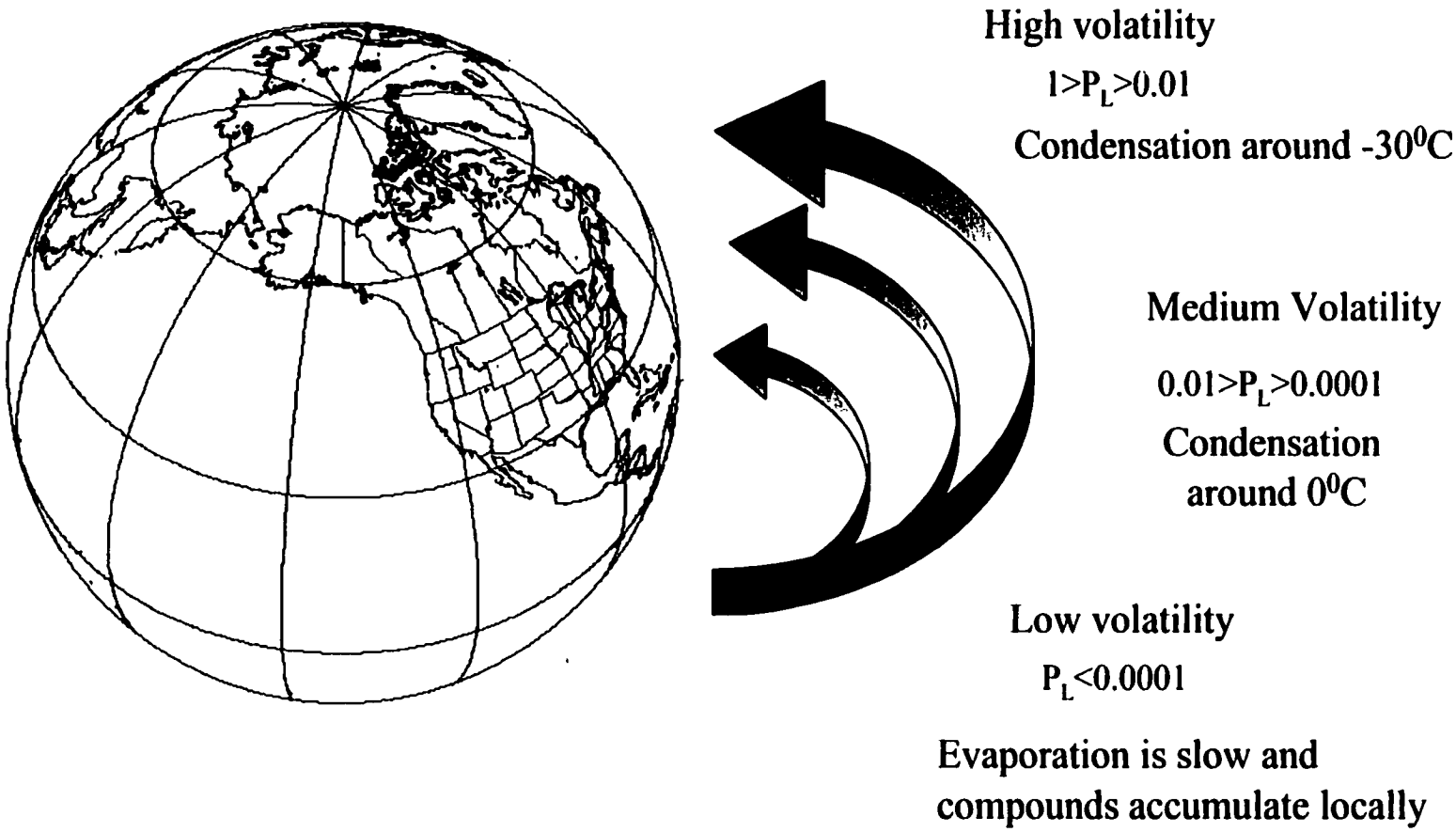

Figure 1.2 Global transport of semi-volatile POPs in the environment, related to the vapour pressure of the subcooled liquid (P_L) at 25°C.

2.0 Distribution of Persistent Organic Pollutants in Lakes of the Canadian Rocky Mountains

2.1 Abstract

Seven lakes spanning a 1430 meter elevation gradient in Alberta and British Columbia, Canada, were sampled for persistent organic pollutants. Bow Lake, Alberta, was sampled over a four-year period (1997-2000) to establish temporal trends of POPs. The other six lakes were sampled over a one or two year period, every two weeks during the summers of 1999 and 2000 to establish seasonal trends of POPs. Hexachlorocyclohexane concentrations in the lakes varied significantly during the spring and summer, generally with highest concentrations in spring following snowmelt. Annual differences in HCH concentrations in Bow Lake, from 1997 through 2000, were correlated with snow pack accumulation ($p<0.001$). Air concentrations were measured at four of the sites with a high volume air sampler, spanning 1205 meters in elevation. Air concentrations of α-HCH and γ-HCH were temperature normalized by the Clausius-Clapeyron equation and were seen to decline between 1998 through 2000 with atmospheric half-lives of 1.4 and 0.8 years, respectively. Air and water concentrations of hexachlorobenzene (HCB) increased at Bow Lake between 1998 – 2000. The present study highlights seasonal and inter-annual trends in air and water concentrations of selected POPs, and demonstrates a relationship between water concentrations of HCHs among years and snow pack accumulation. The observed rise in HCB from 1998 to 2000 corroborates long term data from nearby glacial horizons showing that HCB has been rising steadily in precipitation in this area since the early 1960's.

2.2 Introduction

Persistent organic pollutants such as HCHs, DDTs, chlordanes, endosulfans, PCBs and chlorobenzenes, are semi-volatile compounds that are resistant to rapid degradation in the environment. They are capable of persisting for many years, with half-lives in soils that can range from years to decades (Mackay et al. 1992, 1997). These chemicals can be found as vapours and in condensed phases (water, soil, and sediments) at ambient temperatures and pressures.

POPs travel around the globe by air and ocean currents. Air currents are capable of transporting volatile pesticides such as HCHs and chlordanes half way around the globe within five days (Bailey et al. 2000). POPs are also progressively distilled toward colder environments due to the temperature dependence of their partitioning between air and condensed phases (Wania and Mackay 1993, 1996). In this study, we examine concentrations of POPs in air and water at seven different lakes in the Canadian Rocky Mountains, with an elevation gradient of 1430 meters and a mean summer temperature difference of 10°C. This range in altitude allowed us to examine the distillation of POPs with elevation in lakes spanning a wide gradient of physical parameters such as temperature and precipitation. Due to their remote locations and absence of point source emissions, these lakes receive their chemical input ultimately from the atmosphere.

Five-day back trajectories, for May-August 2000, showed air masses spent most of their time over the Pacific Ocean before arriving at Banff, Alberta (Karen McDonald, Environment Canada, Edmonton, pers. comm.). Donald et al. (1998), found that 5-day back trajectories arriving at Bow Lake originated from the Pacific and Arctic Oceans 60% of the time during the summer months. Air masses at higher altitudes move more

rapidly than air masses at lower altitudes, thus higher sites may receive chemicals that originate from further away (Karen McDonald, Environment Canada, Edmonton, pers. comm.).

High snowfall in these mountain ranges contributes significantly to contaminant loadings into lakes (Blais et al. 2001a). The solubility of a chemical and how it interacts with catchment substrates will influence its movement from the snow pack to the lake during snowmelt (Wania 1997). Chemicals with a higher octanol-water partition coefficient (K_{ow}) will be more likely to adsorb to particulate matter and remain in a lake's catchment during snowmelt. Chemicals with a lower K_{ow} are more water-soluble and partition more into melt water, facilitating transport to lakes. As a result, more water-soluble compounds such as the HCHs may be rapidly transported into these lakes during the spring snowmelt. Hydrophobic compounds such as PCBs and DDTs readily adsorb to particulate matter and are mobilised much more slowly to nearby lakes. Therefore, we might expect POPs with a lower K_{ow} (<4.0) to be mobilised by snowmelt, while POPs with a higher K_{ow} (>5.0) may not show such a relationship.

Using measured concentrations of POPs in air and water samples, collected during the spring and summer of 1999 and 2000, we examined seasonal trends of POPs. Samples were taken at seven lakes located in mountain regions of Alberta and British Columbia. Temporal trends of POPs in air and water, between 1997 through 2000, were examined at Bow Lake. The purpose of this study was to examine how air and water concentrations of POPs were related to elevation, temperature, precipitation, and how they varied among years.

2.3 Materials and Methods

2.3.1 Study Sites

Eight sites were chosen for the collection of water samples, with collection areas (Table 1.1; Fig. 1.1) spanning from Donald Station located at the western edge of the Rocky Mountains, to Dixon Dam Lake located on the prairies, approximately 100 kilometers east of Banff National Park's eastern border. Air samples were collected concurrently with water samples at Bow Lake from 1998 through 2000. In addition, air samples were also collected at Donald Station in 1999 and at Kananaskis and Dixon Dam in 2000. Lake elevations ranged from 770 masl to 2200 masl (Table 1.1), with a mean monthly temperature difference of 10°C between the lowest and highest site, calculated from personal data loggers (Campbell Scientific). Some of these lakes have similar characteristics as arctic and sub-arctic lakes, with a seven to nine month ice cover and low algal and bacterial productivity. Rock Isle, the highest lake in this study, had ice cover for 40 weeks in 1999 and 38 weeks in 2000. Dixon Dam, located on the prairies just west of the town Innisfail, Alberta, is near lindane applications from canola seeding (Fig. 1.1).

2.3.2 Collection of Water Samples

Each lake was sampled every two weeks, from May to August 1997 and 1998, June to August of 1999 and mid-April to August of 2000. For each sampling, approximately 70 litres of water were collected in four 20-L airtight, aluminium cans pre-cleaned with acetone and hexane. Water was taken at the lake surface from the shore. Water temperature and electrical conductivity were measured on site, and water was

filtered through a VWR 1.1μm glass microfiber filter (4.7cm diameter) for electrical conductivity determinations. Filters were ashed by baking for 12 hours at 300 °C in a muffle furnace. The glass microfiber filters were then wrapped in pre-cleaned aluminium foil and stored in plastic bags. Filtering equipment for conductivity measurements was pre-rinsed with Milli-Q water followed by a triple rinse with sample water.

Weather data were collected continuously throughout the sampling period and included relative humidity, barometric pressure, precipitation, wind speed and air temperature. Wind speed was measured with an anemometer located 2 meters above the ground and air temperature was measured with a thermister which recorded measurements to a data logger (Campbell Scientific) every two hours. Data was collected from the shore, near the lakes.

2.3.3 Collection of Air Samples

High-volume air samples (Andersen Samplers inc.) were taken concurrently with water samples at Bow Lake in 1998 through 2000, at Donald in 1999, and at Kananaskis and Dixon Dam in 2000. POPs were extracted from aerosols (on GF/F filters) and from the gas-phase with a 6.4cm x 7.5cm polyurethane foam (PUF) plug, pre-cleaned by Soxhlet extraction with hexane and dichloromethane (DCM). Collected filters and PUF plugs were stored in airtight containers, below 0°C, until they were extracted in the laboratory.

2.3.4 Extraction of Water Samples

Filters, 14.2 cm diameter Whatman GF/F glass microfiber filter (0.7 μm pore) were ashed by baking for 12 hours at 300 °C in a muffle furnace. Filters were then wrapped in pre-cleaned aluminum foil and stored in plastic bags. Water samples were passed through two ashed glass fiber filters using compressed ultra high purity (UHP) nitrogen, on a multiplate filtration manifold. The water was then passed through 250ml of dichloromethane using a Goulden liquid-liquid extractor while being stirred with a stainless steel stirring rod (Goulden and Anthony 1985). Surrogate spiking standards were added concurrently to determine extraction efficiencies (1,3,5- tribromobenzene, 1,2,4,5 - tetrabromobenzene and δ-HCH).

Laboratory glassware and materials were cleaned with laboratory-grade (extran) detergent rinsed with distilled water, then rinsed with wash grade acetone and hexane and baked at 200°C for 10 hours. Both the Florisil and the sodium sulphate were heated prior to use at 600 °C for 16 hours in a muffle furnace. Lab surrogates (PCB 30, PCB 204, 1,3-dibromobenzene and endrin ketone) were added to the samples, followed by solvent exchange into hexane. Samples were evaporated down to 1ml with UHP nitrogen, using a turbo-vap condenser (Zymark II). Analytes of interest were separated into three different fractions, using 1.2% deactivated Florisil (8g) and sodium sulphate (1g) to remove residual water (Muir et al. 1988). The first fraction (37ml of hexane) contained all PCBs, p,p-DDE, p,p-DDD, p,p-DDT as well as 60% of α-HCH, HCB, and the internal standards 1,3-DBB, 1,3,5 - TBB and 1,2,4,5-TTBB. The second fraction (38ml of an 85:15 mixture of (hexane:dichloromethane) contained γ-HCH, heptachlor epoxide, 40% α-HCH and HCB, 45% α-endosulfan and the field surrogate δ-HCH. The third fraction

(52ml of dichloromethane) contained β-endosulfan, dieldrin, methoxychlor, 55% α-endosulfan, as well as the lab surrogate endrin ketone.

Fractions were solvent exchanged into iso-octane and evaporated to 1ml using a turbo vap (Zymark II) (bath temperatures: 35°C at 10 psi for fraction 3, 40°C at 12 psi for fraction 2, 50°C at 18 psi for fraction 1). 20 600 pg of mirex was added as an internal standard to make a concentrations of 106pg μl^{-1}, after each fraction was evaporated to a final volume of 200μl under a gentle stream of UHP nitrogen. A procedural blank, using trace grade DCM, was performed for every eleven samples extracted.

2.3.5 Extraction of Air Sample Filters

All PUF filters were stored frozen until extraction in the laboratory. Each PUF was extracted by refluxing in 300 ml of DCM for 12 hours using Soxhlet. Field surrogates were added to the sample prior to extraction and included: 1,3,5 TBB, 1,2,4,5 TTBB, delta-HCH, PCB 30 and PCB 204. The extract was evaporated to 1 ml using a turbo vap condenser (Zymark II).

The evaporated sample was separated on a Florisil column as described above. Samples were evaporated to 0.5 ml final volumes and mirex was the internal standard, added to make a concentration of 106 pg μl^{-1}. Two blanks were also analyzed and results were blank corrected and surrogate recovery corrected.

2.3.6 Analysis of Water and Air Samples

Samples were injected into a HP 6890 gas chromatograph (GC) for analysis. The GC was equipped with a 30m x 0.25mm DB-5 column with He carrier at 31 cm s^{-1}, and a

^{63}Ni electron capture detector (ECD) with the temperature set at 350°C. One μL of each fraction was injected in the split mode, purge vent off for 30 seconds, using a Hewlett Packard (HP) 7863 series auto-sampler. The injector was set at 220°C and the detector at 350°C. The oven temperature was programmed as follows: 80°C for two minutes, ramping at 10°C min^{-1} to 100°C, and 40°C min^{-1} to 280°C and held for five minutes. Chromatographic data were collected and analyzed using HP Chemstation (Hewlett-Packard, January 1999, Revision A.06.03). A five point calibration set was used to quantify the sample peaks, using mirex as the injection internal standard. All samples were blank corrected and volume corrected using the internal standard mirex. Concentrations were then surrogate corrected using the field surrogates 1,3,5-TBB, 1,2,4,5-TTBB and δ-HCH.

2.3.7 Method Detection Limits

Method detection limits (MDLs) were calculated using the methods by Eaton et al. (1995). The entire suite of OCs was added to 7ml of pure water (OmniSolv) at an estimated MDL, around 2 pg L^{-1}. One ml of this reagent was added to 250ml of DCM and analyzed in the laboratory using the above methods. This process was repeated seven times. The method detection limit of each OC compound was determined by taking the Standard Deviation (S.D) of the 7 independently calculated OC concentrations and multiplying by 3.14 from (Eaton et al. 1995):

$$MDL = S.D * 3.14 \quad (2.1)$$

Where 3.14 is the selected one-sided t distribution for 7-1= 6 degrees of freedom at the 99% level. This process was repeated for the entire suite of PCB congeners. The

instrument detection level (IDL) is estimated at 1:4 the MDL (Eaton et al. 1995). Calculated average water concentrations of most organochlorine compounds and PCBs in this study were above the MDL. Averaged concentrations of DDT congeners were below the calculated MDLs and HCB was occasionally below the MDL in individual samples.

2.3.8 Calculating Atmospheric Half Lives

The Clausius-Clapeyron equation, which describes the relationship between temperature and the gas-phase partial pressures of semivolatile organic compounds, was used to determine environmental phase transition energies of α-HCH, γ-HCH and HCB in the atmosphere:

$$\ln P = -\Delta H/R\ (1/T) + \text{constant} \qquad (2.2)$$

P = partial pressure of the compound (in atm), ΔH = enthalpy of phase transition for the compound (in KJ mol^{-1}), R = the universal gas constant (≅8.314 J. mol^{-1}. K^{-1}), T = absolute temperature in Kelvin. If the introduction of a pesticide into the environment ceases, the decrease in atmospheric concentration is assumed to be first order. Therefore, gas-phase partial pressure can be expressed as a function of both temperature and time with the first order decay equation (Cortes et al 1998):

$$\ln P = a_0 + a_1(1/T) + a_2 \text{ time} \qquad (2.3)$$

$a_1 = -\Delta H/R$ = the slope of the Clausius-Clapeyron plot, setting the first sampling date as day 1, a_2 = a first order elimination rate constant and time is in days. Some variations in pesticide concentrations can be attributed to temperature. To remove this effect and obtain the temperature adjusted pesticide concentrations over time, we adjusted partial pressures to a single temperature using the equation (Cortes et al. 1998).

$$P_{288} = P_{meas} \text{ EXP } (-\Delta H/R(1/288 - 1/T_{meas})) \quad (2.4)$$

P_{288} = the partial pressure of each sample adjusted to 288 Kelvin, P_{meas} = the measured partial pressure, T_{meas} = the 24 hour average temperature measured at each site (in Kelvin), ΔH was determined from a_1 in equation 2.3. Plotting ln P_{288} vs. time (days) gives decreasing air concentrations over time. Corresponding regional atmospheric half-lives were determined using the regression line from the plot.

$$T_{1/2} = \ln(2) / \text{slope} \quad (2.5)$$

Where $T_{1/2}$ is the half-life of the chemical compound in air and slope is the regression line from ln P_{288} vs. time.

2.4 Results

2.4.1 Concentrations of POPs in Water

Water concentrations of γ-HCH decreased from spring to late summer, at most sites, in 1999 and 2000 (Fig. 2.1). Concentration declines with time were significant in 1999 at Rock Isle ($p = 0.029$), Bow Outflow ($p = 0.034$), Vermilion ($p = 0.001$), and Donald ($p = 0.005$) (Table 2.1). In 2000, lindane concentrations declined significantly from April through August at Wapta ($p = 0.033$). A one-way ANOVA revealed that mean water concentrations of γ-HCH were not significantly different between sites in 1999. The data was grouped together and linear regression showed water concentrations of γ-HCH decreased significantly ($p < 0.001$) from June through August in 1999 (Fig. 2.2). Water concentrations of γ-HCH were not correlated with altitude or temperatures in either 1999 or 2000.

Lindane concentrations decreased at Rock Isle and Vermilion Lakes while electrical conductivity increased, during both the 1999 and 2000 field seasons (Fig. 2.1). At Rock Isle, concentrations of γ-HCH decreased from 602 pg L^{-1} on July 2, 1999 to 174 pg L^{-1} on August 18, 1999 while conductivity rose from 88 μS cm^{-1} to 155 μS cm^{-1} over the same time interval. Similar results were seen at Vermilion when concentrations of γ-HCH decreased from 550 pg L^{-1} on April 18, 2000 to 185 pg L^{-1} on August 8, 2000 while conductivity rose from 310 μS cm^{-1} to 650 μS cm^{-1}, over the same time interval (Fig. 2.1).

Mean water concentrations of total PCBs were significantly lower in 2000 compared with the 1999 season, $p< 0.05$ (Fig. 2.3). Water concentrations of total PCBs were observed to decline at Bow Lake from 1998-2000 ($p= 0.14$) (Tables 2.2, 2.3).

Mean water concentrations of the α-endosulfan and β-endosulfan isomers were higher in the Bow Glacial stream compared to the Bow Outflow site, 1997-2000 (Table 2.2, 2.3). Average water concentrations of the β-endosulfan isomer were consistently higher than the α-endosulfan isomer at all of the sites, except at Bow Lake in 1998 (Table 2.2). The ratio of β-endosulfan: α-endosulfan in water was consistently in the range 1.15 -1.30 at all sites and between years (Table 2.2).

Average water concentrations of HCHs were lower in 2000 than in 1999 (Table 2.2; Fig. 2.4, 2.5), with declines for α-HCH ranging from 6% at Rock Isle to 65% at Bow Glacial stream and declines for γ-HCH ranging from 37% at Rock Isle to 88% at Wapta. Snow pack was also lower in 2000 compared to 1999 (Table 2.4). In addition, summer precipitation at Bow Lake was 34% greater in 1999 compared to 2000 (Table 2.4). Trends between water concentrations of HCHs and snow pack at Bow Lake were not so

apparent when comparing averages between 1997-2000. However, measurements taken by Blais et al. (1998) showed that concentrations of γ-HCH were much higher in snow compared to water, at Bow Lake (Fig. 2.6). Concentrations of both the α-HCH and the γ-HCH isomers were highest in 1999, the year of highest snowfall (Table 2.2, 2.3).

2.4.2 Concentrations of POPs in Air

Air concentrations of α-HCH fluctuated considerably during both the summer of 1999 and 2000 (Table 2.5). In 1999, concentrations ranged from 6.4 pg m^{-3} to 47 pg m^{-3} at Bow Lake and 8.7 pg m^{-3} to 36 pg m^{-3} at Donald Station (Table 2.5). In 2000, air concentrations of α-HCH ranged from 3.2 pg m^{-3} to 64 pg m^{-3} at Bow Lake, from 4.4 pg m^{-3} to 98 pg m^{-3} at Kananaskis and from 3.7 pg m^{-3} to 29 pg m^{-3} at Dixon Dam (Table 2.5).

The partial pressure of α-HCH at 288K (P_{288}) decreased significantly ($p<0.05$), from 1998 to 2000 at Bow Lake (Table 2.6, 2.7; Fig. 2.7, 2.8). Most of the decrease in average air concentrations of α-HCH took place between 1999 and 2000 (Table 2.8), indicating these are fluctuating concentrations and not long-term trends.

In 1998, air concentrations of γ-HCH peaked in the spring and then decreased as the summer progressed (Fig. 2.5). However, this trend did not occur at Bow Lake in 1999 or 2000 (Table 2.7; Fig. 2.5). From 1998 – 2000, air concentrations of lindane declined with an atmospheric half-life of 0.7± 0.2 years at Bow Lake (Table 2.6; Fig. 2.7, 2.8). Average concentrations fell progressively over the three years ranging from 20± 17 pg m^{-3} SD in 1998, 8.1± 5.1 pg m^{-3} in 1999 and 2.3± 1.6 pg m^{-3} SD in 2000 (Table 2.8). A high air concentration (120 pg m^{-3}) of γ-HCH was observed at the Dixon Dam site, on

July 10th, 2000 (Table 2.5). This site is located beside farmland and the high concentration may have reflected a very recent and near-by application of lindane.

Average concentrations of HCB in air increased dramatically at Bow Lake between 1998 and 2000 (Table 2.7, 2.8). Average concentrations were 8.7± 4.4 pg m^{-3} in 1998, 17 ± 11 pg m^{-3} during the summer of 1999, and 42 ± 12 pg m^{-3} S.D during the summer of 2000. This is an average increase of 480% over the three year period with an approximate doubling time of 0.9 years (Table 2.6).

Air concentrations of β-endosulfan were found to be considerably lower than air concentrations of α-endosulfan at all sites (Table 2.5,2.7). The concentrations of the two isomers were not significantly correlated with temperature or elevation (Table 2.5, 2.7).

Atmospheric concentrations of heptachlor epoxide and dieldrin were found at very low levels at all of the sites and concentrations remained steady from spring through summer (Table 2.5). Using the Clausius-Clapeyron equation, it was found that air concentrations of heptachlor epoxide and dieldrin did not change significantly at Bow Lake from 1998-2000, however concentrations of dieldrin increased steadily over the three year period (Tables 2.6, 2.7).

2.5 Discussion

2.5.1 Water Concentrations of POPs

The declining concentrations of γ-HCH with concurrent increasing electrical conductivity, at Rock Isle Lake and Vermilion Lake, suggests higher lindane release during spring snowmelt (Fig. 2.1). During snowmelt ions such as: K^+, Ca^+, Mg^+, Na^+ and Cl^- become more diluted from ionically weak snowmelt runoff, therefore decreasing

conductivity in lakes (Stottlemyer and Toczydlowski 1996; Laudon et al. 2000). Following the snowmelt pulse, ion rich groundwater and runoff water contribute to a higher observed conductivity indicating snowmelt is over (Stottlemyer and Toczydlowski 1996).

The only site that did not show decreasing lindane concentrations, from spring to late summer, was the Bow Glacial stream (Fig. 2.1). Melt water from the Bow Glacier shifts from snowmelt in spring to glacial melt as snow cover disappears (Blais et al. 2001a). Lindane is released into the Glacial Stream with the snowmelt pulse in the spring and continues to be released into the stream with glacial melt during the summer. Wania (1997) estimated that around 60% of lindane remains in glacial ice after the first year of snow settling, while 40% is lost to volatilization. In general, lindane accumulates in glacial ice layers during firnification and is later released into glacial streams as glaciers melt. In accordance with this model, the Bow Glacial stream did not show a seasonal trend in γ-HCH concentrations but displayed steady lindane concentrations throughout the summer.

A plausible explanation for higher concentrations of HCHs in water in 1999 is the deeper snow pack compared with 1997, 1998 and 2000 (Table 2.4; Fig. 2.5). Atmospheric HCHs are found mainly in the vapour phase and they are fairly water soluble. As a consequence, vapour phase HCHs are readily scavenged by snow (Atlas and Giam 1988), making snow an important contributor to lake water concentrations. Therefore, a larger snow pack in 1999, compared to 1997, 1998 and 2000 (Table 2.4), is a plausible explanation for the larger flux of HCHs into the lakes for that year (Table 2.4).

Decreasing concentrations of γ-HCH from spring to late summer may be attributed to a large input of lindane into the lakes during spring snowmelt. This trend was most pronounced in 1999, the year with the highest snow fall (Table 2.4; Fig. 2.2). Semkin (1996) and Wania et al. (1999), found spring snowmelt to be an important contributor of OCs to surface waters. γ-HCH is readily scavenged by falling snow (Atlas et al. 1998; Czuczwa et al. 1988) and accumulates in the snow pack throughout the winter. The compound migrates down through the snow pack and is eluted early during snowmelt (Wania 1997). It has been estimated that during snow melting only 2% of γ-HCH in a snow pack is lost to volatilization, while 98% partitions into the aqueous phase and is drained with melt water (Wania 1997). This caused a large concentrated pulse of γ-HCH, and to a lesser extent α-HCH, into the lakes during snowmelt (Table 2.3; Fig. 2.1 and 2.2).

A study at Amituk Lake (Barrie et al. 1997), located on the eastern coast of Cornwallis Island, also found a large input of γ-HCH into the lake in the spring followed by a steady decline throughout the summer. A steady-state model indicated that from 80% to 99% of γ-HCH contained in the winter snow pack entered the lake during snowmelt and was eventually exported from the lake before the end of the summer (Barrie et al. 1997). Volatilization losses were generally less than 5% of total loading, indicating that arctic lakes may act more as fluvial conduits for HCHs.

Another possible explanation for the declining concentrations of lindane in the lakes as the summer progressed would be an increase in degradation rates as temperatures and daylight hours both increased. Photo-oxidation rate constants for lindane in isolated surface waters has been recorded with a half-life of 270 days (Mackay and Choi 1995),

which could account for a loss of 1.8 grams from Bow Lake, from May to August in 2000. Loss from outflow was calculated at 4.7 grams over the same time interval.

The decreasing concentrations of lake water PCBs observed in this region of the Rocky Mountains may be an ongoing process as it is in other areas of Canada (Table 2.3; Fig. 2.3). The calculated half-life of PCBs at Bow Outflow was 1.8 years and 1.5 years for the Bow Glacial Stream. These half-lives are comparable to others that have been calculated for Lake Superior. Jeremiasson et al. (1994) observed that concentrations of 25 PCB congeners in Lake Superior decreased from 1980 to 1992 with a half-life of 3.5 years. A mass balance of PCBs in Lake Superior showed that most of this loss was due to volatilization (Jeremiasson et al. 1994). Smith (2000) found that PCBs in the water column in Lake Superior decreased by about 23% each year and water column concentrations had decreased, from 1980 to 1996, with a half-life of 3.1 years.

Consistently lower concentrations of the endosulfan isomers were observed at the Bow Outflow site, 1997-2000, compared to the glacial stream. The lower concentrations at the Bow Outflow site suggests that the Bow Glacial stream is an important contributor of endosulfan to the lake (Blais et al. 2001b). Water concentrations of β-endosulfan were consistently higher than α-endosulfan (Table 2.2), despite α and β-endosulfan being applied in a 7:3 parts mixture. The consistently higher water concentrations of the β-endosulfan isomer compared to the α-endosulfan isomer, may be a function of its relatively lower Henry's law constant (Table 1.2). β-endosulfan is about 5.7-fold more water soluble than α-endosulfan and is readily scavenged by precipitation (Rice et al. 1997). The ratio of α-endosulfan:β-endosulfan in air ranged from 10 – 50, while the ratio

in water was approximately 0.82. These ratios clearly show that α-endosulfan stays mainly in air while β-endosulfan partitions into waters.

2.5.2 Air Concentrations

Air concentrations of α-HCH declined at Bow Lake between 1998 through 2000 with a half-life of 1.4 years (Table 2.6; Fig. 2.7, 2.8). These declines were only short term trends, but were found to be significant ($p=0.04$). More accurate half-lives require at least ten years of data. Air concentrations of α-HCH have also been found to be declining elsewhere; with calculated half-lives of 4 years in the Great Lakes basin (Cortes et al. 1998), and Haugen et al. (1998) recorded air concentrations that declined with a half life of 4 years at Lista, southern Norway. The lack of temperature sensitivity observed for atmospheric α-HCH (Table 2.5; Fig. 2.4) suggests that these chemicals were derived primarily by long range transport (Haugen et al. 1998, 1999; Wania et al. 1998; Bailey et al. 2000). In remote areas, local revolatilization of POPs from land or water surfaces is generally not an important process controlling air concentrations (Bailey et al. 2000), because of the relatively low concentrations of contaminants stored in soil and sediment compared to more urbanised and agricultural areas.

In 1998 air concentrations of γ-HCH at Bow Lake were at their maximum in the spring and declined as the summer progressed (Fig. 2.5), a trend that may have been related to canola seeding in Alberta and Saskatchewan. Others have also found peak air concentrations of lindane in the spring that coincided with seeding, in Quebec (Poissant et al. 1996) and in Ontario (Ridal et al. 1996). However, air vapour concentrations of γ-HCH, in 1999 and 2000, were not at their maximum in the spring following seeding and

concentrations were not significantly correlated with temperature ($p = 0.457$) (Table 2.5, 2.7; Fig. 2.5). Planting of lindane treated canola seeds in Manitoba, Saskatchewan and Alberta remained unchanged from 1998 through 2000 (Don Waite, Env. Can., Regina, pers. comm.), thus the declines that we observed may be explained by declining lindane applications in other countries, such as the United States (Mark Howard, U.S EPA, pers. comm.; NAWQA 2001; NPUD 2001; PISU 2001).

Decreased lindane concentrations in air during the spring of 1999 and 2000 may have been partly related to low soil moisture during seeding (Waite et al. In prep). Using high volume air samplers, Waite et al. (In prep) found drastically lower air concentrations of γ-HCH near canola fields (south central Saskatchewan) planted with treated seed in 1998, compared to 1997. This was despite increased use of lindane in 1998. Estimated volatilisation losses from crops were 30% in 1997 over a 5-week period but only 12% in 1998 over a 6-week period because of lower precipitation. Ehlers et al. (1969 a,b), measured γ-HCH volatilisation from soil and found it was negligible in soils with 1% moisture content and increased proportionately up to 3% moisture content.

Air concentrations of lindane have been found to decline in other parts of Canada as well. In the Great Lakes region, calculated atmospheric half-lives of γ-HCH range from 2.2 years at Lake Michigan to 7.3 years at Lake Ontario (Cortes et al. 1998). Atmospheric half-lives at Bow Lake were calculated at 0.8 years between 1998 to 2000 (Table 2.6; Fig. 2.7, 2.8). We expect air concentrations of lindane will continue to decrease at Bow Lake in the future because of its recent ban in Canada (Don Waite, Env. Can., Regina, pers. comm.).

Five-day back trajectories of air masses for Banff, Alberta, indicated that at higher altitudes (500 mbar pressure) most of the air masses started from the eastern Pacific Ocean (Fig. 2.9). At lower altitudes (850 mbar pressure) back trajectories showed that five days prior to air sampling, air masses were located closer to the sampling site; this included the Mid Pacific, the Canadian Arctic and eastern Alberta (Fig. 2.9). This may account for variability in atmospheric concentrations of POPs between sites such as Bow Lake and Dixon Dam (Table 2.5). The source of air masses would in turn influence water concentrations of POPs as well.

The observed increase in air concentrations of HCB could be a result of delayed atmospheric transport to this region. Donald et al. (1999), found concentrations of HCB in dated glacial horizons that increased at a relatively constant rate from 1959 to 1995 at Snow Dome Glacier in Alberta, Canada. In addition, six lake sediment cores taken along a mid-continental transect, 49°N to 82°N, showed HCB increased from 1960-1990 (Barrie et al. 1997). HCB is a by-product from the manufacturing of other chlorinated products and is released into the environment from the application of pesticides contaminated with HCB (Environment Canada, 1997a). It is also released from incineration, leachates from hazardous waste landfills and from industrial emissions. Because HCB is highly volatile (Table 1.3), long range transport plays a significant role as a continuing source to the Canadian environment (CEPA 1993).

Although water concentrations of β-endosulfan were consistently 15-30% higher than the α-endosulfan isomer (Table 2.2), air concentrations of β-endosulfan were much lower than α-endosulfan (Tables 2.5, 2.7). Technical endosulfan is used in the ratio 7:3 α-endosulfan:β-endosulfan (NRCC 1975), which partly explains why air concentrations

of α-endosulfan are higher than β-endosulfan. There is also evidence that β-endosulfan is photochemically converted to α-endosulfan in air (Rice et al. 1997). In addition, β-endosulfan more readily partitions out of air and deposits onto land and water surfaces. When examining endosulfan in air, Burgoyne and Hites (1993) considered the α-endosulfan isomer to be the major isomer of importance, while β-endosulfan was usually below the detection limit.

2.6 Conclusions

This study has demonstrated the significance of snowmelt as a major source of lindane to lakes located in the Canadian Rocky Mountains. Major inputs of lindane into the lakes occurred via runoff from snowmelt in late spring, resulting with a peak in the spring followed by declining lindane concentrations as the summer progressed. Both α-HCH and γ-HCH showed a surge in water concentrations in 1999 compared with 1998 and 2000, which may be explained by the higher snow pack that year. In 1998 air concentrations of lindane were highest in the spring at Bow Lake and decreased throughout the summer. This did not occur in 1999 or 2000, which indicated decreased uses from nearby sources. Air concentrations of both α-HCH and γ-HCH were found to decline significantly at Bow Lake between 1998-2000. Concentrations of lindane should continue to decline in the future at these sites because it was banned in Canada, beginning July 1st of 2001. Declining water concentrations of PCBs at Bow Lake, 1998 through 2000, most likely reflects a long-term trend that has also been observed in other parts of Canada and the world. Because of their volatility, long range transport from other countries is the main source of HCBs to this region of Canada. This affects concentration

levels in the region studied. The observed increase in both air and water concentrations of HCB at Bow Lake, from 1998 through 2000, may be a result of delayed deposition from long range transport. Concentrations of α-endosulfan were found to be higher in air but lower in water relative to β-endosulfan levels. The 10-50 times higher levels of α-endosulfan in air can be partly explained by its higher rate of application, at 7:3 α-endosulfan:β-endosulfan. In addition, β-endosulfan is photochemically converted to α-endosulfan in air and β-endosulfan is more likely to deposit onto terrestrial surfaces. The higher levels of the β-endosulfan isomer in water can be explained by its' approximately 5.7-fold higher liquid phase solubility compared to α-endosulfan. World use of the POPs examined in this study has decreased over the last few decades, and more recently for the HCHs. Concentrations of POPs usually show sharp decreases, near source areas, immediately after uses are discontinued. Concentrations then equilibrate as POPs are redistributed in the environment.

Table 2.1 Table of linear regressions for γ-HCH concentrations in lake waters vs. time. (days).

Year	Site	Altitude	P value	R^2	Slope	S.E of Slope
1999	Rock Isle	2200	0.029*	0.84	-7.7	2.0
2000	Rock Isle	2200	0.075	0.86	-4.3	1.3
1999	Bow Glacial	1975	0.87	0.011	0.62	3.4
2000	Bow Glacial	1975	0.64	0.048	-0.35	0.7
1999	Bow Outflow	1975	0.034*	0.72	-6.5	2.0
2000	Bow Outflow	1975	0.092	0.55	-0.43	0.2
1999	Wapta	1590	0.13	0.47	-28	15
2000	Wapta	1590	0.033*	0.63	-1.3	0.45
1999	Vermilion	1380	0.001*	0.96	-11	1.2
2000	Vermilion	1380	0.28	0.23	-2.1	1.7
1999	Donald	770	0.005*	0.89	-12	2.2
2000	Kananaskis	1667	0.061	0.63	-0.63	0.24
2000	Dixon Dam	940	0.62	0.066	1.0	1.9

* P<0.05

Table 2.2 Averaged water concentrations (Standard Deviations in brackets) of selected organochlorines and total PCBs at eight different locations ranging in altitude from 770 to 2200 masl. Sample collection spanned from May – August in 1997 and 1998, June-August in 1999 and from April – August in 2000. All concentrations are in pg L^{-1}. HCH is hexachlorocyclohexane, HCB is hexachlorobenzene and ∑PCBs are the sum of 130 polychlorinated biphenyls.

Location and Date	α-endosulfan	β-endosulfan	α-HCH	γ-HCH	HCB	Hept. Epoxide	Dieldrin	∑ PCBs
Year- 1997								
Bow Glacial	19 (15)	25 (8.7)	220 (100)	110 (81)	5.7 (2.4)	8.2 (3.0)	22 (10)	N/A
Bow Outflow	7.4 (4.2)	20 (11)	140 (60)	57 (17)	4.6 (2.1)	3.2 (1.8)	12 (6.5)	N/A
Year - 1998								
Bow Glacial	16 (14)	9.9 (4.7)	230 (110)	150 (55)	7.3 (4.6)	9.8 (3.6)	22 (12)	460 (360)
Bow Outflow	5.7 (1.7)	3.6 (0.5)	130 (46)	83 (34)	5.4 (1.5)	3.8 (1.0)	9.4 (3.1)	310 (310)
Year – 1999								
Rock Isle	63 (130)	80 (170)	340 (110)	350 (170)	18 (6.9)	20 (7.3)	17 (14)	180 (84)
Bow Glacial	50 (29)	60 (34)	400 (88)	280 (130)	28 (21)	23 (8.6)	43 (26)	140 (46)
Bow Outflow	15 (6.6)	19 (8.2)	470 (130)	410 (200)	19 (3.5)	18 (6.2)	16 (15)	120 (61)
Wapta	25 (13)	30 (15)	88 (28)	610 (100)	18 (6.3)	9.0 (3.0)	13 (5.1)	170 (79)
Vermilion	0.28 (0.69)	0.37 (0.9)	370 (90)	560 (300)	13 (4.5)	8.9 (2.2)	9.5 (14)	160 (96)
Donald	15 (16)	19 (20)	180 (61)	390 (330)	16 (6.7)	7.6 (7.5)	14 (19)	170 (89)
Year – 2000								
Rock Isle	100 (90)	120 (110)	320 (160)	220 (130)	17 (6.5)	12 (5.7)	18 (5.0)	110 (37)
Bow Glacial	39 (42)	46 (50)	140 (130)	120 (65)	16 (1.8)	13 (6.7)	26 (13)	110 (45)
Bow Outflow	19 (15)	23 (18)	210 (43)	130 (24)	21 (17)	7.5 (6.7)	22 (5.0)	94 (30)
Kananaskis	15 (7.9)	17 (9.4)	160 (31)	140 (29)	15 (5.0)	5.5 (3.3)	12 (3.5)	110 (45)
Wapta	21 (8.9)	25 (11)	44 (29)	73 (65)	17 (11)	4.7 (2.6)	7.9 (6.4)	97 (21)
Vermilion	26 (21)	31 (25)	230 (110)	280 (170)	25 (22)	2.9 (2.2)	5.5 (8.1)	130 (47)
Dixon	20 (20)	23 (23)	74 (13)	530 (150)	12 (6.4)	5.8 (4.4)	5.5 (3.4)	94 (66)

Table 2.3 Water concentrations (pg L^{-1}) of selected organochlorines and sum of all PCBs (Σ PCBs) at Bow Outflow, from 1997-2000. Hept. Epox. is heptachlor epoxide.

Date	α-endosulfan	β-endosulfan	α-HCH	γ-HCH	HCB	Hept. Epox.	Dieldrin	Σ PCBs
June 6, 97	4.5	10	120	62	3.5	1.2	17	N/A
June 20, 97	3.5	7.7	110	46	3.0	1.6	4.5	N/A
July 1, 97	4.2	16	88	43	5.1	2.9	9.7	N/A
July 13, 97	5.5	12	110	45	4.4	3.4	6.7	N/A
July 29, 97	15	36	250	87	8.8	6.1	23	N/A
Aug. 10, 97	7.8	28	110	43	2.7	2.5	8.3	N/A
Aug. 24, 97	12	29	200	71	4.4	5.0	12	N/A
Averages	7.4	20	140	57	4.6	3.2	12	N/A
S.D.	4.2	11	60	17	2.1	1.8	6.5	N/A
May 10, 98	7.2	3.0	69	35	4.3	1.8	8.9	790
May 20, 98	6.0	4.0	150	60	5.3	2.5	8.3	290
June 8, 98	4.0	3.0	57	44	2.8	2.1	4.3	110
June 24, 98	0	4.0	110	95	3.1	3.5	6.8	120
July 26, 98	7.7	0	140	94	4.8	3.9	8.5	150
Aug. 9, 98	5.7	3.8	70	46	4.9	3.1	5.2	230
Aug. 26, 98	3.5	3.5	110	64	3.4	3.4	6.7	150
Averages	5.7	3.6	130	83	5.4	3.8	9.4	310
S.D.	1.7	0.46	46	34	1.5	1.0	3.1	310
June 4, 99	20	23	580	730	23	24	37	220
June 16, 99	0	0	630	380	21	24	0	65
June 30, 99	20	24	340	480	16	13	24	67
July 17, 99	3.8	4.5	500	480	16	21	0	94
July 31, 99	12	14	460	240	16	12	20	150
Aug. 11, 99	21	26	310	160	23	11	13	150
Averages	15	18	470	410	19	18	16	120
S.D.	6.6	8.2	130	200	3.5	6.2	15	61
Apr. 25, 00	10	12	280	160	16	0	22	100
May 30, 00	6.3	7.5	180	160	56	18	29	140
June 13, 00	12	15	180	120	11	8.7	14	70
June 28, 00	12	14	190	110	16	8.9	20	60
July 27, 00	45	53	250	130	11	0	22	82
Aug. 15, 00	28	34	200	100	19	10	25	110
Averages	19	23	210	130	21	7.5	22	94
S.D.	15	18	43	24	17	6.7	5	30

Table 2.4 Precipitation and snow pack at Bow Lake for the years 1997 through 2000. SWE stands for snow-water equivalent in millilitres and exhaustion from met is the date snow pack was no longer measurable at the Bow Lake weather station.

Year	Precipitation (mm)	Temperature (°C)	March 30 (SWE mm)	May 30 (SWE mm)	Date of Complete Snow Pack Melt
1997	182	8.34	462	254	N/A
1998	221	10.4	257	0	May 2
1999	233	8.0	460	329	May 30
2000	155	8.0	434	239	May 23

Table 2.5 Air concentrations (Standard Deviations for each data set in brackets) of selected organochlorines and total PCBs at altitudes ranging from 770 to 2000 meters above sea level (masl). Samples were taken with a high-volume air sampler (Anderson Inc.) spanning June-August in 1999 and May-August in 2000. Concurrent air temperatures were taken with a data logger every two hours. HCH is hexachlorocyclohexane, HCB is hexachlorobenzene, Hept. Epox. is heptachlor epoxide and ∑PCBs are the sum of 130 polychlorinated biphenyls.

Concentrations (pg m^{-3})

Location and Date	α-endosulfan	β-endosulfan	α-HCH	γ-HCH	HCB	Hept. Epox.	Dieldrin	∑ PCBs
Bow								
June 4, 99	47	1.3	37	13	6.5	1.7	0.48	12
June 16, 99	47	0.2	47	11	21	1.2	1.4	17
June 30, 99	16	1.3	6.4	0	33	0	1.4	66
July 28, 99	17	0.01	46	6.2	8.1	0.24	0.22	14
Aug. 11, 99	14	0.1	43	11	16	0.38	0.38	18
Averages	**28 (17)**	**0.56 (0.68)**	**36 (17)**	**8.1 (5.1)**	**17 (11)**	**0.73 (0.47)**	**0.77 (0.57)**	**25 (23)**
Donald								
June 10, 99	1.3	0	23	0.51	20	0.25	0.03	77
June 23, 99	53	7.2	8.7	1.8	22	0.5	2.9	210
July 7, 99	4.0	0.12	36	5.8	20	0.24	0.08	77
July 20, 99	19	0.04	30	17	6.2	0.74	0.6	70
Aug. 4, 99	26	0.4	34	16	6.3	2.0	0.61	110
Averages	**21 (21)**	**1.6 (3.2)**	**26 (11)**	**8.3 (7.9)**	**15 (7.8)**	**0.74 (0.72)**	**0.84 (1.2)**	**110 (57)**
Bow								
May 9, 00	36	1.2	3.2	0.4	54	0.2	0.9	280
June 1, 00	24	2.0	14	3.2	53	2.0	3.3	80
June 28, 00	26	4.5	64	4.3	44	2.2	2.5	49
July 25, 00	13	0.1	17	2.3	24	0	0.3	240
Aug 15, 00	32	6.3	6.7	1.0	36	0	2.3	89
Averages	**26 (9.0)**	**2.8 (2.3)**	**21 (25)**	**2.3 (1.6)**	**42 (12)**	**0.88 (1.12)**	**1.9 (1.2)**	**150 (100)**
Kananaskis								
May 5, 00	470	3.8	98	0.9	200	11	13	580
May 19, 00	480	52	16	0	27	11	11	620
June 22, 00	17	1.6	4.4	0.3	24	0.1	1.1	77
July 12, 00	180	14	43	0	60	3.9	6.1	490
Aug. 7, 00	17	2.3	4.9	0.5	19	0	0.9	320
Averages	**230 (230)**	**15 (21)**	**33 (39)**	**0.3 (0.4)**	**66 (77)**	**5.3 (5.6)**	**6.2 (5.3)**	**420 (220)**
Dixon								
May 29, 00	4.5	0	3.7	0	37	0	0.2	180
July 10, 00	35	4.2	29	120	15	3.1	2.9	95
July 31, 00	53	10	9.9	1.2	39	2.4	6.6	250
Averages	**31 (25)**	**4.8 (5.2)**	**14 (13)**	**40 (69)**	**30 (14)**	**1.8 (1.6)**	**3.2 (3.2)**	**170 (75)**

Table 2.6 Increases and decreases in air concentrations of selected pesticides were calculated using the equation $\ln P = a_0 + a_1(1/T) + a_2$ time. a_1 is the slope of the Clausius-Clapeyron Plot (ln P vs. 1000/T), which calculates changing concentrations as a function of temperature. P is the partial pressure of the chemical of interest, in (atm). T is temperature in Kelvin and a_2 is a first order rate constant. a_1 was used to calculate the temperature normalized partial pressures of the chemicals of interest (P_{288}). The slopes of the lines from the graphs ln P_{288} vs. time (in days) were used to calculate increasing or decreasing concentrations over time, $T_{1/2} = \ln 2/\text{slope}$. γ-HCH is gamma-hexachlorocyclohexane, α-HCH is alpha-hexachlorocyclohexane and HCB is hexachlorobenzene.

Compound	a_1	Slope of ln P_{288} vs. Time (Days)	Half-Lives and Doubling Times (Years)
γ-HCH	-11*	-0.0024	T ½ = 0.7
α-HCH	-9.7**	-0.0014	T ½ = 1.4
HCB	8.7*	0.0022	T double = 0.9
Dieldrin	7.8	0.0016	No change
α-endosulfan	0.82	-0.0016	No change
β-endosulfan	10	-0.0024	No change
Heptachlor epoxide	-3.8	0.0001	No change

*P<0.05, **P<0.01

Table 2.7 Air concentrations, in pg m^{-3}, (Standard Deviations for each data set in brackets) of selected organochlorines and total PCBs at Bow Lake (1975 masl) for the years 1998, 1999 and 2000. Samples were taken with a high-volume air sampler (Anderson Inc.) spanning May –August in 1998, June-August in 1999 and May-August in 2000. Concurrent air temperatures were taken with a data logger every two hours. HCH is hexachlorocyclohexane, HCB is hexachlorobenzene, and Hept. Epox. is heptachlor epoxide.

Date	Temp. (C)	α endo-sulfan	β endo-sulfan	α-HCH	γ-HCH	HCB	Hept. Epox.	Dieldrin
May 18, 98	5.1	6.9	0	33	45	15	0	0.3
June 6, 98	6.7	0.3	0.1	36	46	5.7	0.2	0.9
June 22, 98	11.3	16	0.2	40	15	8.6	1.3	0.3
July 4, 98	10.9	23	0.3	46	22	5.6	0.9	0.8
July 27, 98	11.9	12	0	45	2.9	6.5	2.3	0.9
Aug. 8, 98	15	17	0	22	7.2	3.4	1.0	0.1
Aug. 25, 98	15	22	0.8	37	6.9	13	0.5	0.3
Averages	**11.4**	**14**	**0.35**	**36**	**21**	**8.7**	**0.88**	**0.47**
S.D.		**(8.3)**	**(0.27)**	**(7.8)**	**(20)**	**(4.4)**	**(0.85)**	**(0.34)**
June 4, 99	3.7	47	1.3	37	13	6.5	1.7	0.48
June 16, 99	10.0	47	0.2	47	11	21	1.2	1.38
June 30, 99	4.4	16	1.3	6.4	0	33	0	1.4
July 28, 99	7.1	17	0.01	46	6.2	8.1	0.24	0.22
Aug. 11, 99	8.6	14	0.1	43	11	16	0.38	0.38
Averages	**8.2**	**28**	**0.56**	**36**	**8.1**	**17**	**0.73**	**0.77**
S.D.		**(17)**	**(0.68)**	**(17)**	**(5.1)**	**(11)**	**(0.47)**	**(0.57)**
May 9, 00	-1.1	36	1.2	3.2	0.4	54	0.2	0.9
June 1, 00	1.5	24	2.0	14	3.2	53	2.0	3.3
June 28, 00	9.4	26	4.5	64	4.3	44	2.2	2.5
July 25, 00	9.5	13	0.1	17	2.3	24	0	0.3
Aug 15, 00	5.6	32	6.3	6.7	1.0	36	0	2.3
Averages	**8.4**	**26**	**2.8**	**21**	**2.3**	**42**	**0.88**	**1.9**
S.D.		**(8.9)**	**(2.3)**	**(25)**	**(1.6)**	**(12)**	**(1.1)**	**(1.2)**

Table 2.8 Average air concentrations, in pg m^{-3}, (Standard Deviations for each data set in brackets) of alpha hexachlorocyclohexane (α-HCH) gamma hexachlorocyclohexane (γ-HCH), hexachlorobenzene (HCB), dieldrin, α-endosulfan and β-endosulfan at Bow Lake (1975 masl) for the years 1998, 1999 and 2000. Samples were taken with a high-volume air sampler (Anderson Inc.) spanning May –August in 1998, June-August in 1999 and May-August in 2000. Concurrent air temperatures were taken with a data logger every two hours, and averaged for the sampling period.

Year	Air Temp. (°C)	α-HCH	γ-HCH	HCB	Dieldrin	α-endosulfan	β-endosulfan
1998	11.4	36 (7.8)	21 (20)	8.7 (4.4)	0.47 (0.34)	14 (8.3)	0.35 (0.27)
1999	8.2	36 (17)	8.1 (5.1)	17 (11)	0.77 (0.57)	28 (17)	0.56 (0.68)
2000	8.4	21 (25)	2.3 (1.6)	42 (12)	1.9 (1.2)	26 (8.9)	2.8 (2.3)

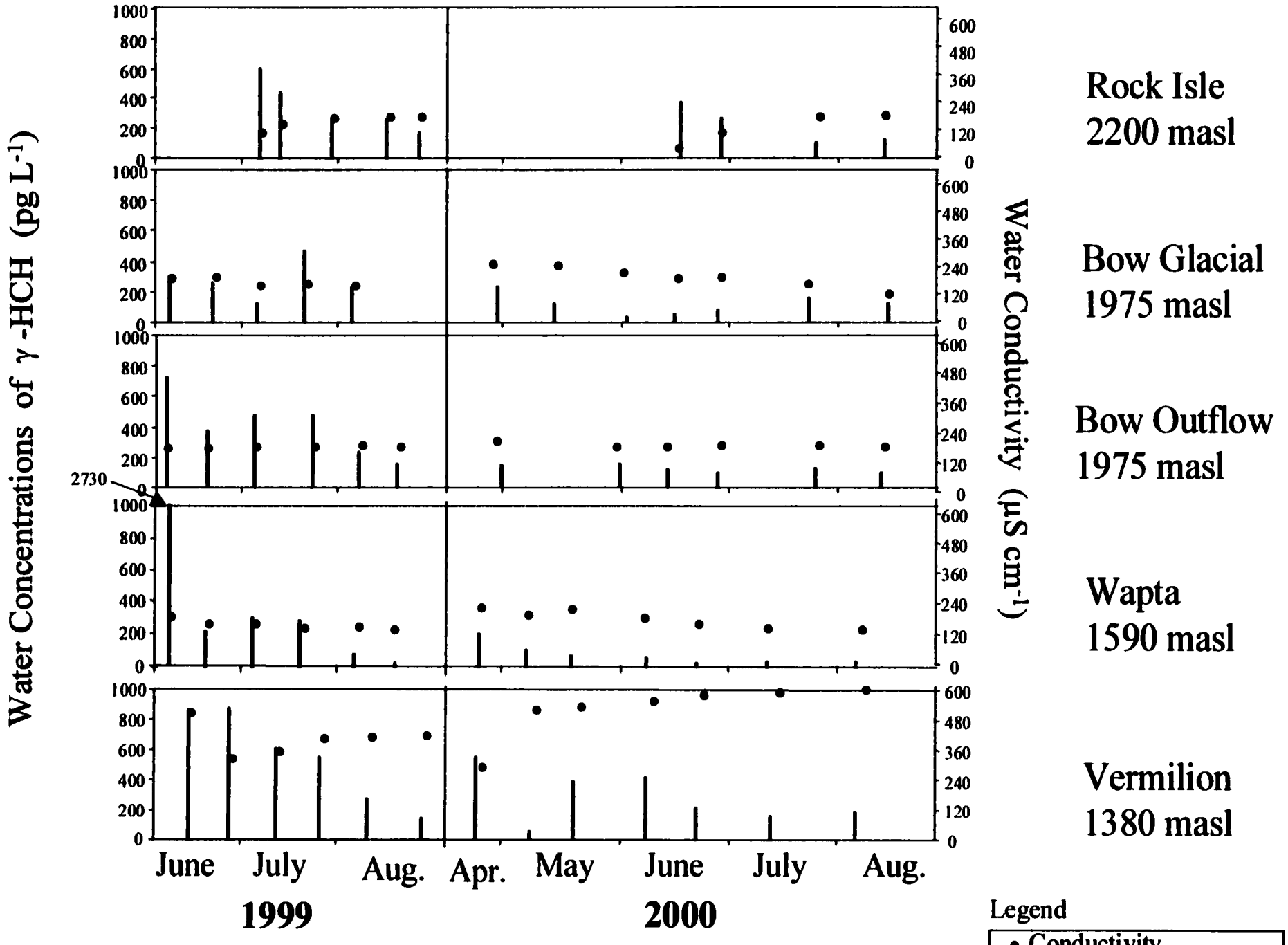

Figure 2.1 Water concentrations of γ-HCH at five different study sites. Water concentrations decreased from June-August in 1999 and from April-August in 2000.

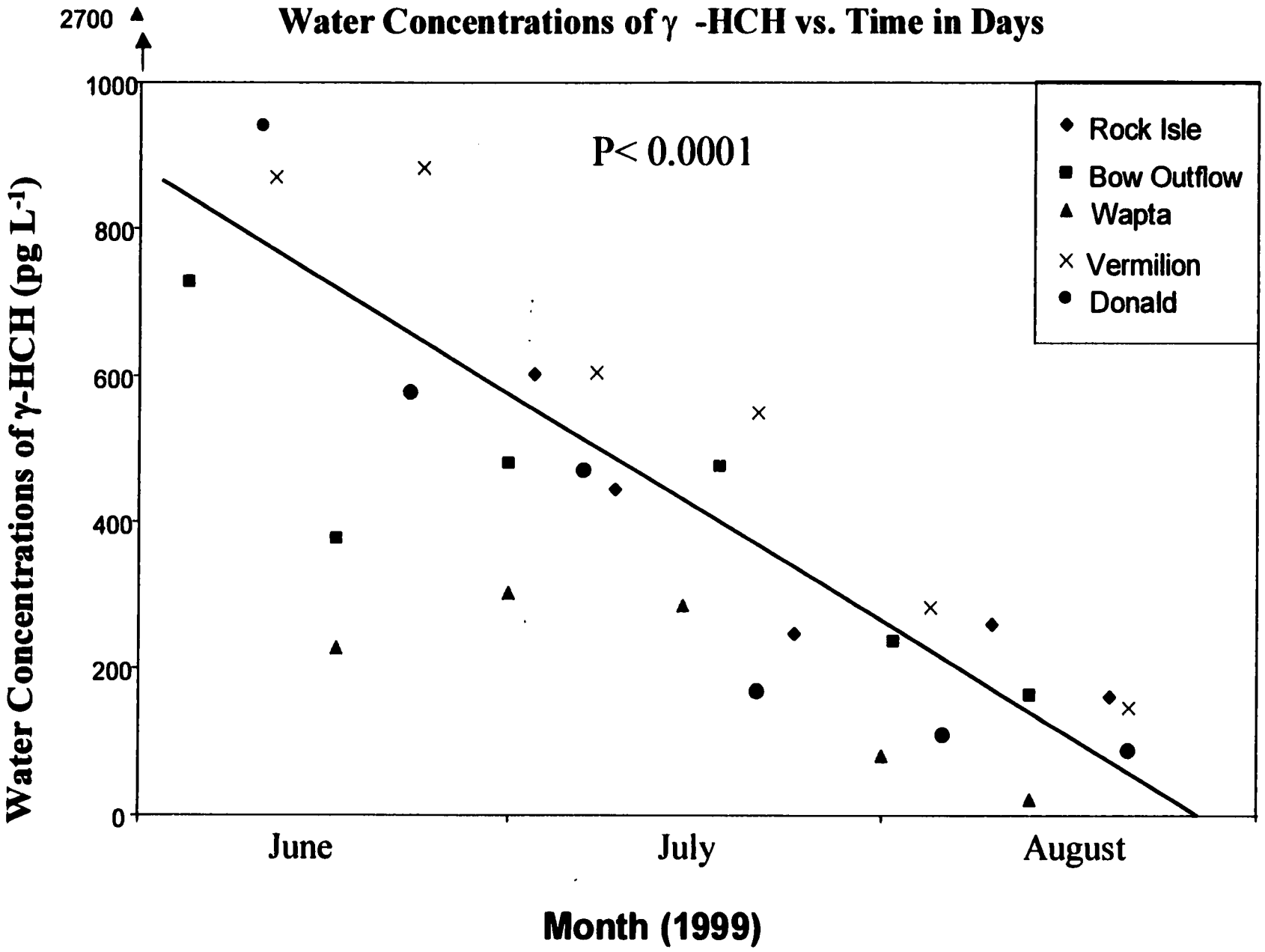

Figure 2.2 Water concentrations of γ-HCH decreased significantly, from June through August in 1999, at five of the study sites.

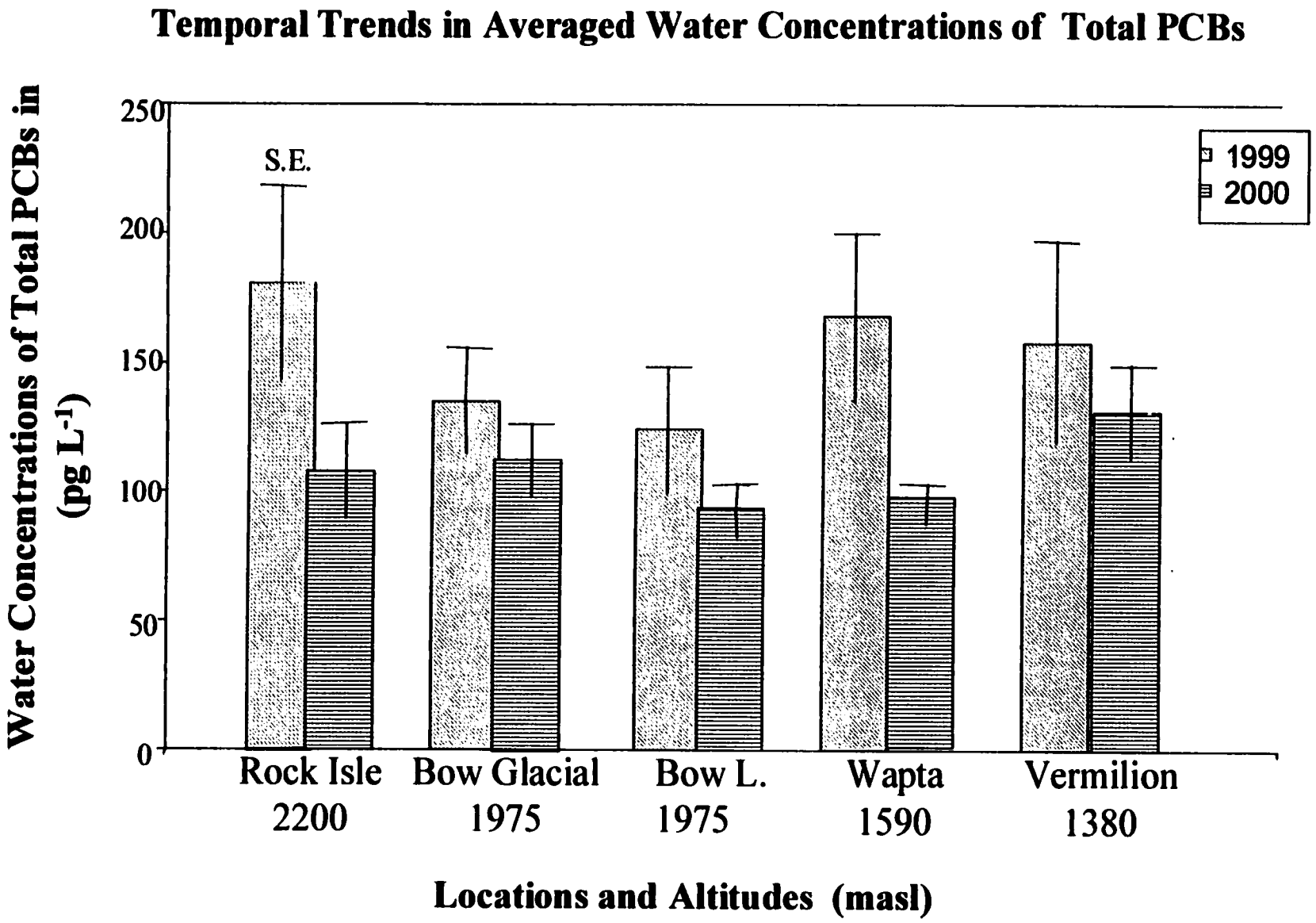

Figure 2.3 Averaged concentrations of PCBs in (pg L^{-1}), from five study sites. Mean concentrations decreased significantly between 1999 and 2000, p=0.018.

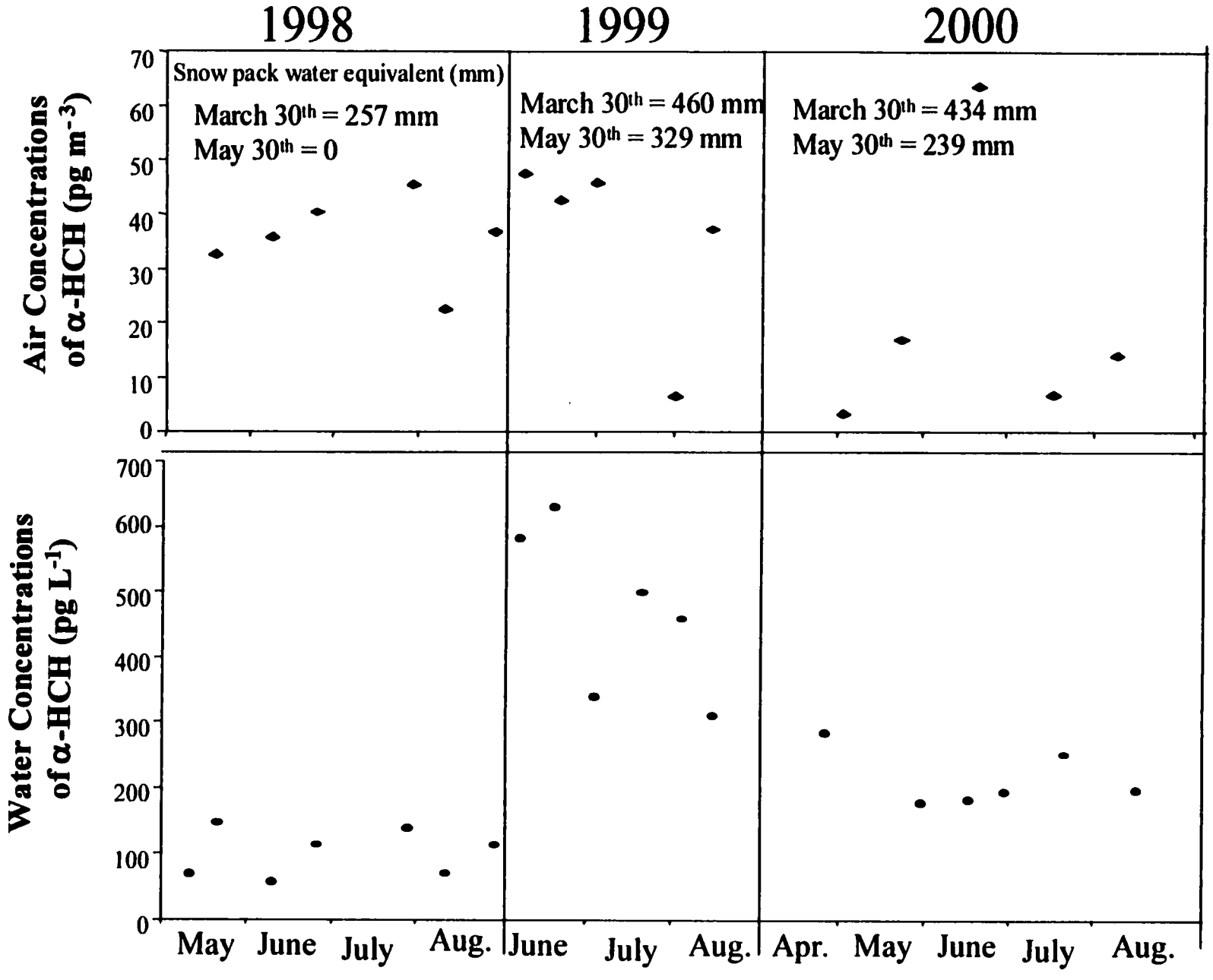

Figure 2.4 Air and water concentrations of α-HCH at Bow Lake, 1998 through 2000. Air concentrations of α-HCH showed no correlation with temperature. Water concentrations of α-HCH were higher during years with higher snow pack and decreased with time in 1999.

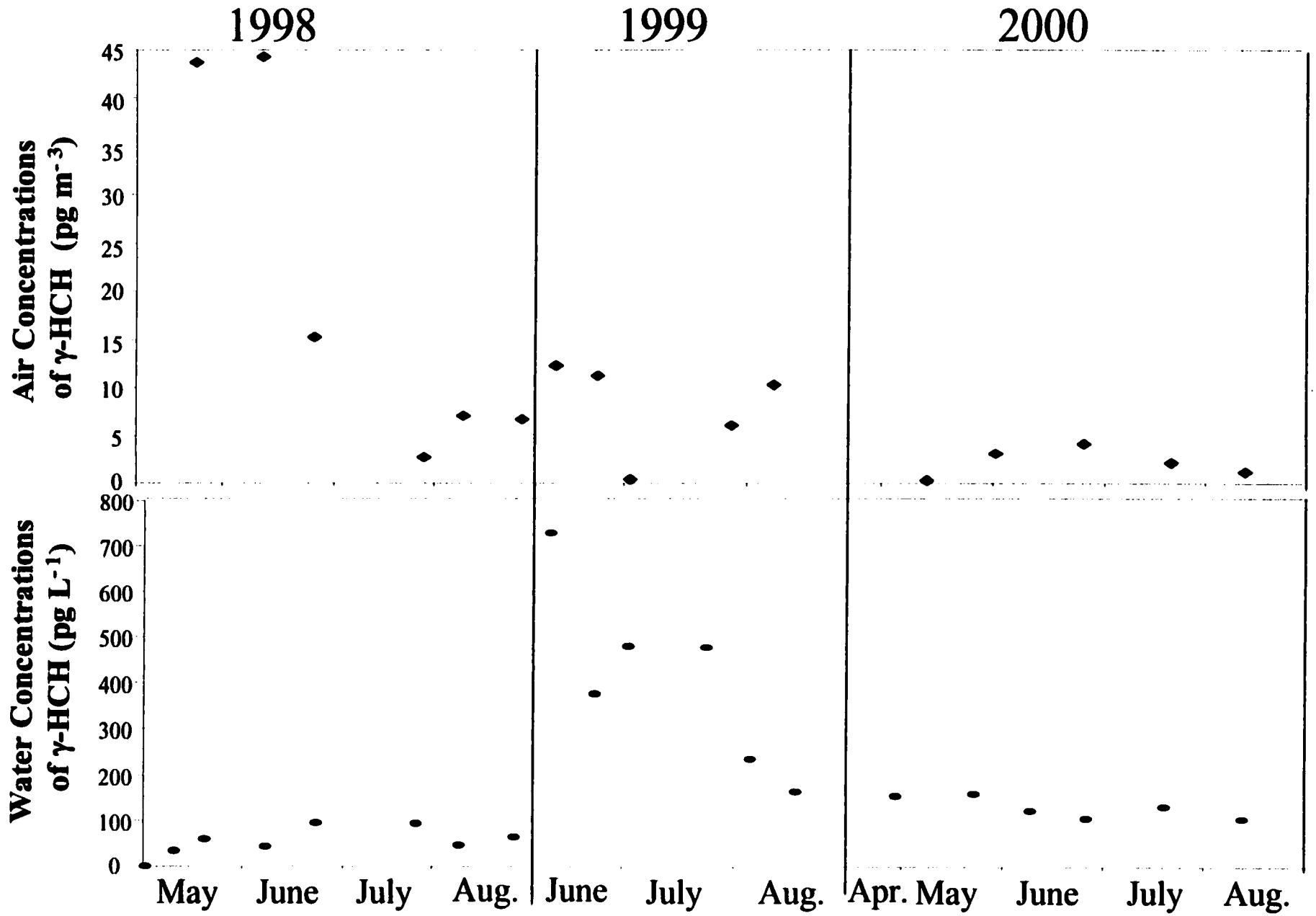

Figure 2.5 Air and water concentrations of γ-HCH at Bow Lake, 1998 through 2000. Air concentrations of γ-HCH showed steady declines over the three year period. Water concentrations of γ-HCH were higher during years with higher snow pack and decreased significantly from June through August in 1999.

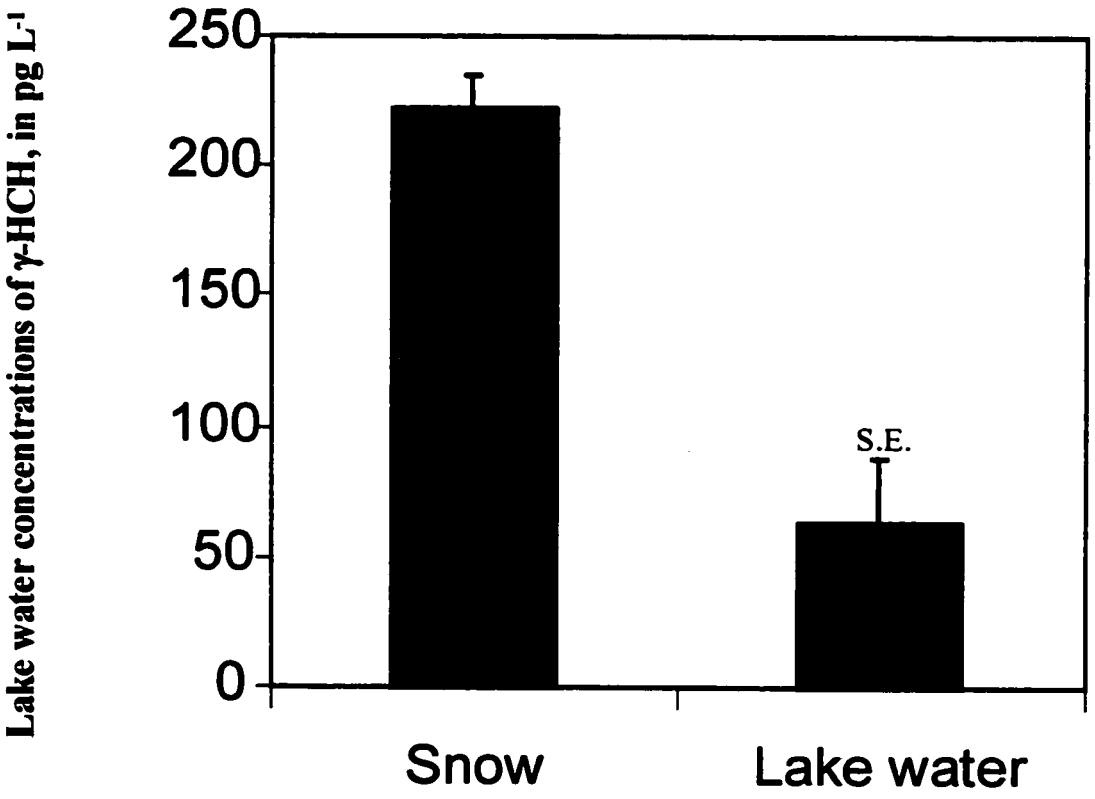

Figure 2.6 Concentrations of γ-HCH (pg L^{-1}) in snow and lake water from Bow Lake, 1998.

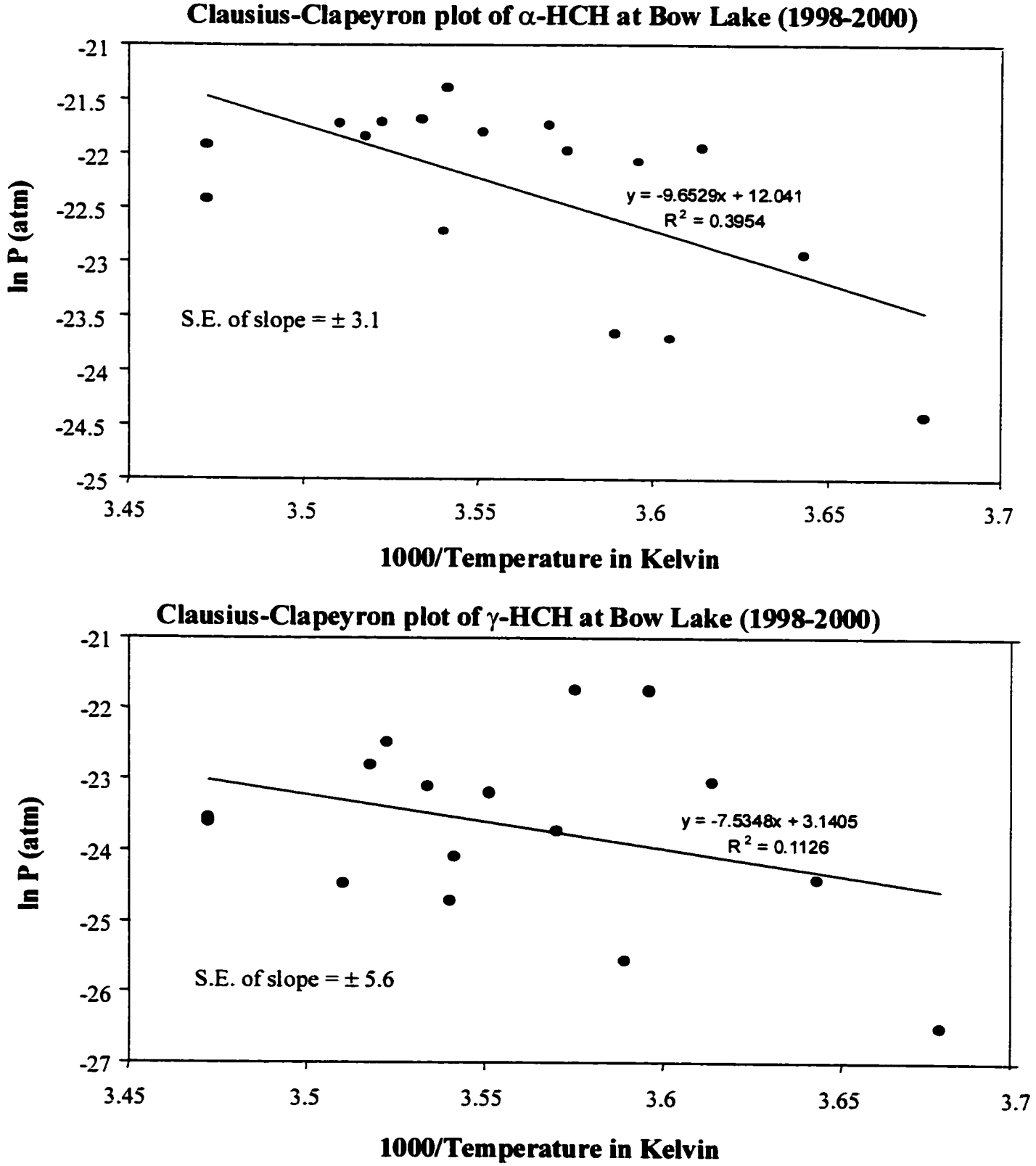

Figure 2.7 Clausius-Clapeyron plots of α-HCH and γ-HCH at Bow Lake, from 1998-2000.

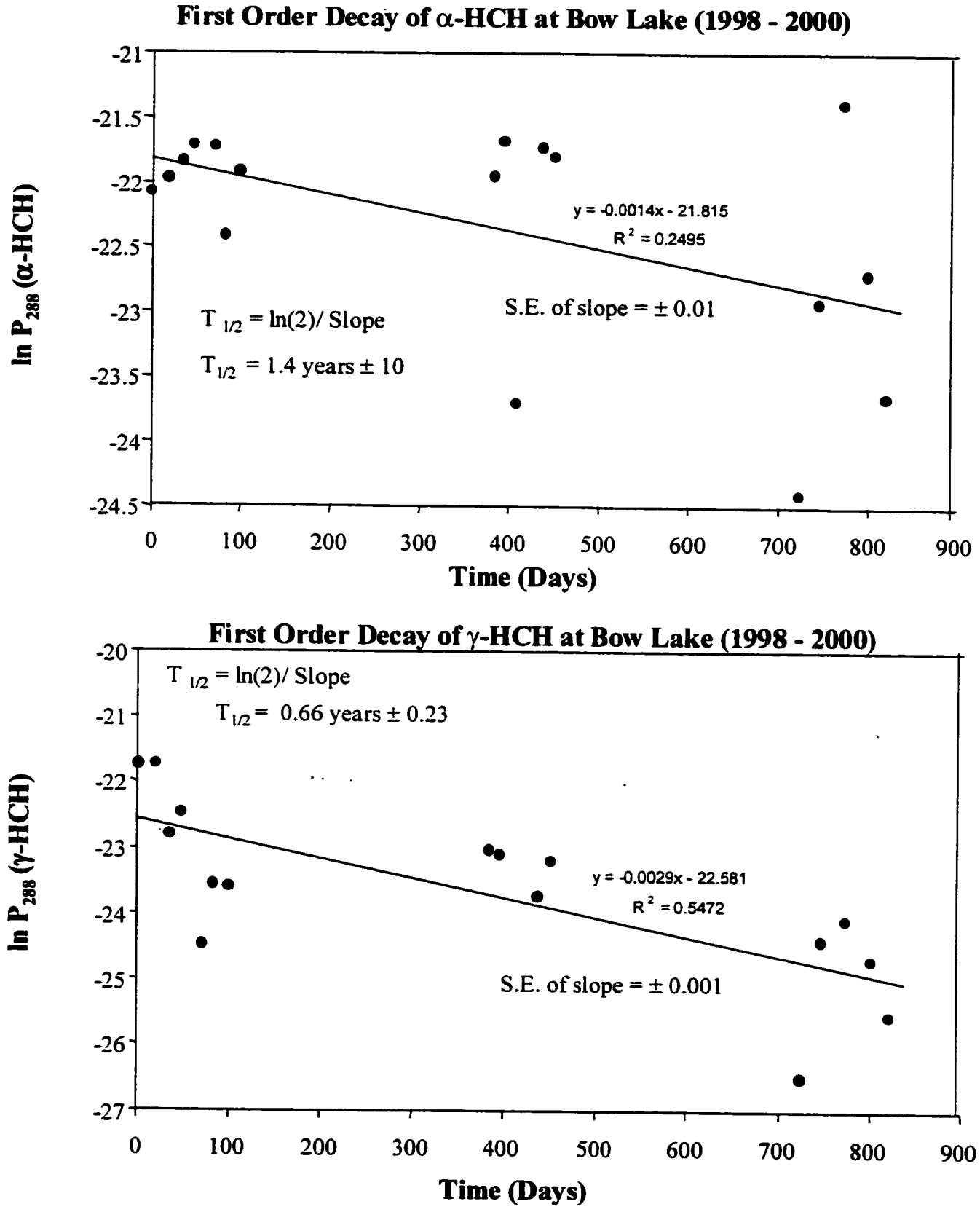

Figure 2.8 First order decay graphs of α-HCH and γ-HCH at Bow Lake, 1998-2000. Graphs are used to calculate half lives of compounds in air.

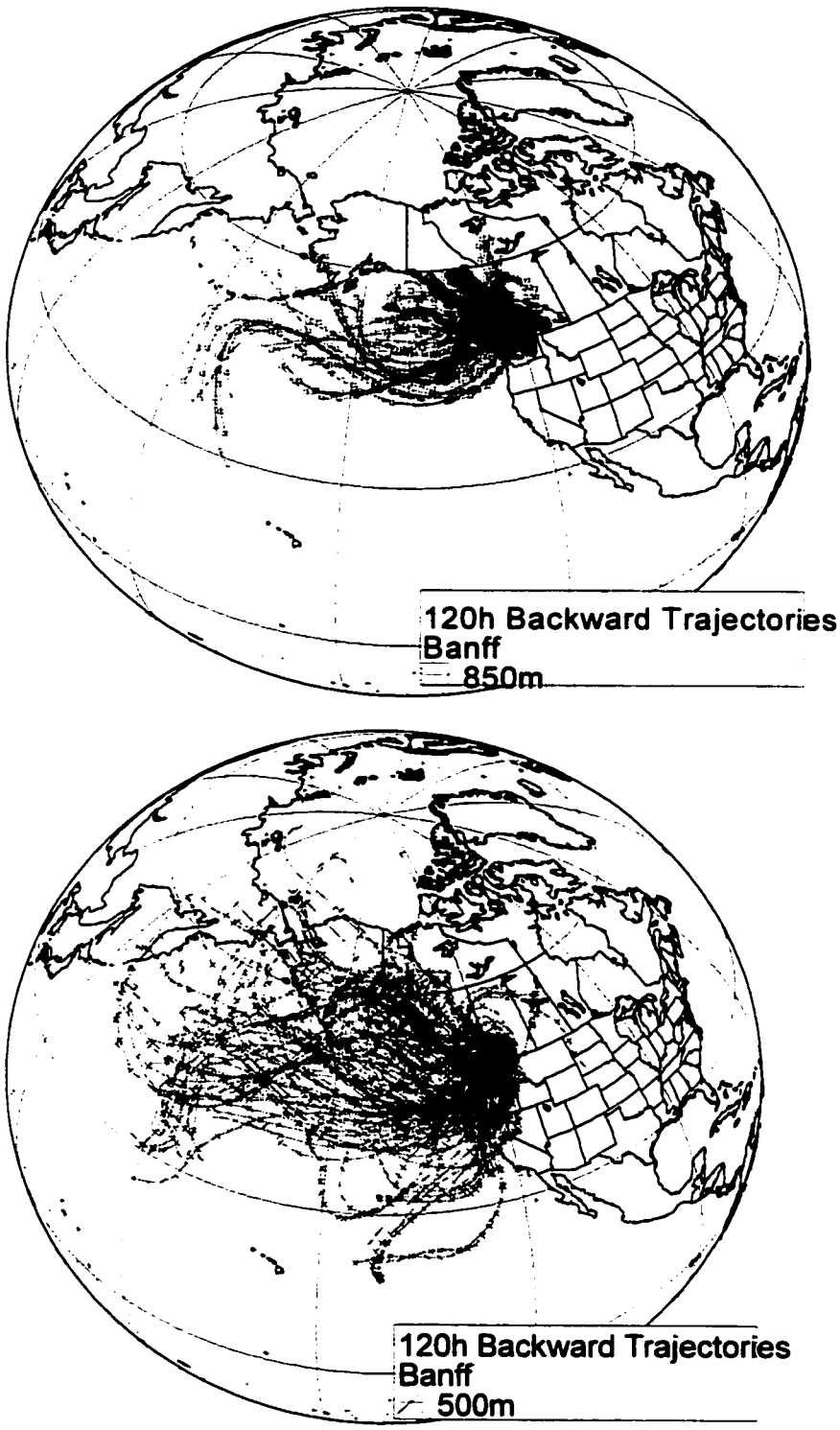

Figure 2.9 Five day back trajectories of air masses at Banff, calculated for different atmospheric pressures. Atmospheric pressure decreases with increasing elevation. Pressure is in Milli-bar (m).

3.0 Air-Water Gas Exchange of Chlorinated Pesticides in Several Lakes Spanning from the Interior Plains to the Western Range of the Canadian Rocky Mountains

3.1 Abstract

Concentrations of selected persistent organic pollutants (POPs) in air and water were measured from four lakes that transect the Canadian Rocky Mountains, from the Interior Plains of Alberta to the Western Range of the Rockies in British Columbia. These data were used in combination with wind velocity and temperature-adjusted Henry's law constants to estimate the direction and magnitude of gas flux across the air-water interface of these lakes. Samples were collected during the spring and summer at Bow Lake (1998-2000), Donald Station (1999), Kananaskis Lake (2000) and Dixon Dam Lake (2000). Bow Lake was oversaturated with respect to the air in hexachlorobenzene (HCB), dieldrin and β-endosulfan and thus the direction of flux was from water to air for these chemicals for all three years. Evaporation rates for the three years were 5.1 ±1.9, 1.9 ±0.82 and 1.2 ±0.95 ng m^{-2} d^{-1} for HCB, dieldrin and β-endosulfan, respectively. Water concentrations of α-endosulfan were undersaturated with respect to air, and the rate of deposition into water for the three years was 11.5 ±5.7 ng m^{-2} d^{-1}. Direction of gas exchange for alpha hexachlorocyclohexane (α-HCH) varied between years at Bow Lake, but had a net deposition of 3.7 ±10.4 ng m^{-2} d^{-1} when averaged over the three summers. The average direction of γ-HCH exchange at Bow Lake shifted from net deposition in 1998 to net volatilization in 1999 and 2000. Average air concentrations declined steadily over the three year period, from 21 pg m^{-3} in 1998 to 2.3 pg m^{-3} in 2000, causing air to become undersaturated with respect to the water in 1999 and 2000. Air and

water concentrations of the organochlorine compounds (OCs) were not significantly correlated with elevation. When comparing air-water exchange with the lakes' storage and losses by outflow, it was shown that air-water gas exchange was an important influence on the overall storage of HCB, dieldrin and endosulfans in these lakes, but less important for α and γ-HCH.

3.2 Introduction

Atmospheric transport of persistent organic pollutants such as hexachlorocyclohexanes (HCHs), polychlorinated biphenyls (PCBs), hexachlorbenzene and toxaphene have contaminated arctic (Norstrom et al. 1988; Barrie et al. 1992; Wania and Mackay 1993; Bidleman et al. 1995) and alpine environments (Blais et al. 1998; Donald et al. 1998; Grimalt et al. 2001). Some semi-volatile pollutants are evaporated from warmer source regions and then atmospherically transported and deposited in colder areas, a process termed "global distillation" (Goldberg 1975; Wania and Mackay 1993, 1996).

Atmospheric inputs are important sources of POPs to water bodies located in remote areas (Jantunen and Bidleman 1995, 1996; McConnell et al. 1996; Blais et al. 2001). This includes wet deposition, dry deposition and deposition from air-water gas exchange. Air-water gas exchange occurs in both directions so it can act both as a source of POPs to lakes through net deposition and as a loss by volatilization. In general, net deposition across the air-water interface has been found for chemicals with higher Henry's law constants such as the HCHs (McConnell et al. 1996), while net volatilization has been reported for less water-soluble compounds like dieldrin (Blais et

al. 2001b), HCB (McConnell et al. 1996) and most PCBs (Jeremiasson et al. 1994, 1999; McConnell et al. 1996).

Concentrations of HCHs, HCB, endosulfans, and dieldrin were determined simultaneously in air and surface waters from four lakes, spanning from the Interior Plains in Alberta to the Western Range of the Rockies, in order to determine the relative contributions by air-water gas exchange. Estimates of net fluxes across the air-water interface were determined using the two-film resistance model originally developed by Whitman (1923), and later modified by Schwarzenbach et al. (1993). This model envisions a stagnant layer of air about 1mm in thickness and a stagnant layer of water approximately 0.1mm in thickness, at the air-water interface. Concentrations of chemicals in the boundary layers of air and water are intermittently mixed by diffusion, therefore are different from their uniformly mixed bulk volumes (Schwarzenbach et al. 1993). The difference in the concentration gradient between the two phases is what drives the direction of the chemical transfer (Whitman 1923). The overall rate of chemical transfer is controlled by the rate of transport through the two boundary layers, therefore the stagnant layer with the highest resistance to mass transfer determines the total resistance to mass transfer between the bulk water and air (Schwarzenbach et al. 1993).

The goals of this study were to estimate the direction and magnitude of chemical transport across the air-water interface for a range of chemicals (HCHs, HCB, dieldrin and endosulfans) from lakes spanning an elevation gradient of 1205 meters. Estimates of atmospheric deposition onto these lakes, or volatilization from these lakes, were calculated during the ice free seasons. These results were compared with outflow losses

in order to determine the significance of air-water gas exchange to total inventories of POPs in these lakes. It has been suggested that the more volatile organochlorines may be concentrating in colder alpine lakes because of temperature influences on air-water gas exchange (Grimalt et al. 2001).

3.3 Materials and Methods

3.3.1 Study Sites

The Canadian Rocky Mountains are characterized by a vast wilderness located in rugged terrain, with high climatic variability. This mountain range is 1450km in length, spanning from the Liard River in Northern British Columbia to the international boundary in the south and it runs 150km in width from the Rocky Mountain Trench in the west to the Interior Plains in the east (Gadd 1995). Elevation ranges from 305 (masl), confluence of the Liard and Toad rivers (BC), to 3450 masl, Mt. Robson (AB) (Schmidt 1986).

Air and water samples were collected from four different sites spanning the width of the Canadian Rockies, with an elevation gradient of 1205 meters between the lowest and highest sites. Donald (770 masl), located in the Western Range of the Rockies, is characterized by a moist temperate climate (Gadd 1995). Dixon Dam (946 masl), located in agricultural plains100 kilometers east of the mountain parks near the town of Innisfail, has a dryer and slightly cooler climate. Bow Lake (1975 masl) and Kananaskis Lake (1667 masl) experience cool and wet conditions because of their higher elevations. Air samples were collected concurrently with water samples at Bow Lake from 1998 through 2000, at Donald Station in 1999 and at Kananaskis and Dixon Dam in 2000.

3.3.2 Water Sampling

Each lake was sampled every two weeks, from May through August 1997 and 1998, June through August of 1999 and May through August of 2000. For each sampling, approximately 70 litres of water were collected in four 20-L airtight, aluminium cans pre-cleaned with acetone and hexane. Water temperature and dissolved organic carbon were measured on site, and water was filtered through a VWR 1.1μm glass microfiber filter (4.7cm diameter) for DOC determinations. Filters were ashed by baking for 12 hours at 300 °C in a muffle furnace. The glass microfiber filters were then wrapped in pre-cleaned aluminium foil and stored in plastic bags. Filtering equipment for DOC measurements was pre-rinsed with Milli-Q water followed by a triple rinse with sample water.

Weather data were collected continuously throughout the sampling period and included relative humidity, barometric pressure, precipitation, wind speed and air temperature. Wind speed was measured with an anemometer located 2 meters above the ground and air temperature was measured with a thermister which recorded measurements to a data logger (Campbell Scientific) every two hours.

3.3.3 Air Samples

High-volume air samples (Andersen Samplers Inc.) were taken concurrently with water samples during the ice free season at Bow Lake (1998 through 2000), at Donald Station (1999), and at Kananaskis Lake and Dixon Dam (2000). POPs were extracted from aerosols (on GF/F filters) and from the gas-phase with a 6.4cm x 7.5cm polyurethane foam (PUF) plug, pre-cleaned by Soxhlet extraction with hexane and

dichloromethane (DCM). Collected filters and PUF plugs were stored in airtight containers, below 0°C, until they were extracted in the laboratory.

3.3.4 Extraction of Water Samples

Filters, 14.2 cm diameter Whatman GF/F glass microfiber filter (0.7 μm pore) were ashed by baking for 12 hours at 300 °C in a muffle furnace. Filters were then wrapped in pre-cleaned aluminum foil and stored in plastic bags. Water samples were passed through two ashed glass fiber filters using compressed ultra high purity (UHP) nitrogen, on a multiplate filtration manifold. The water was then passed through 250ml of dichloromethane using a Goulden liquid-liquid extractor while being stirred with a stainless steel stirring rod (Goulden and Anthony 1985). Surrogate spiking standards were added concurrently to determine extraction efficiencies (1,3,5- tribromobenzene, 1,2,4,5 - tetrabromobenzene and δ-HCH).

Laboratory glassware and materials were cleaned with laboratory grade (extran) detergent rinsed with distilled water, then rinsed with wash grade acetone and hexane and baked at 200°C for 10 hours. Both the Florisil and the sodium sulphate were heated prior to use at 600 °C for 16 hours in a muffle furnace. Lab surrogates (PCB 30, PCB 204, 1,3-dibromobenzene and endrin ketone) were added to the samples, followed by solvent exchange into hexane. Samples were evaporated down to 1ml with UHP nitrogen, using a turbo vap condenser (Zymark II). Analytes of interest were separated into three different fractions using 1.2% deactivated Florisil (8g) and sodium sulphate (1g) to remove residual water (Muir et al. 1988). The first fraction (37ml of hexane) contained all PCBs as well as p,p-DDE, p,p-DDD, p,p-DDT, 60% α-HCH, HCB and the internal

standards 1,3-DBB, 1,3,5 - TBB and 1,2,4,5-TTBB. The second fraction (38ml of an 85:15 mixture of hexane:dichloromethane) contained γ-HCH, heptachlor epoxide, 40% α-HCH, HCB, 45% α-endosulfan, and the field surrogate δ-HCH. The third fraction (52ml of dichloromethane) contained β-endosulfan, dieldrin, methoxychlor and 55% α-endosulfan, as well as the lab surrogate endrin ketone.

Fractions were solvent exchanged into iso-octane and evaporated to 1ml using a turbo-vap (Zymark II) (bath temperatures: 35°C at 10 psi for fraction 3, 40°C at 12 psi for fraction 2, 50°C at 18 psi for fraction 1). Fractions were evaporated to a final volume of 200μl, under a gentle stream of UHP nitrogen, and 20 600pg of mirex was added as an internal standard (106 pg μl^{-1}). A procedural blank, using trace grade DCM, was performed for every eleven samples extracted.

3.3.5 Extraction of Air Sample Filters

All PUF filters were stored frozen until extraction in the laboratory. Each PUF was extracted by refluxing in 300 ml of DCM for 12 hours using a Soxhlet apparatus. Field surrogates were added to the sample prior to extraction and included: 1,3,5 -TBB, 1,2,4,5 -TTBB, δ-HCH, PCB 30 and PCB 204. The extract was evaporated to 1 ml using a turbo vap condenser (Zymark II).

The evaporated sample was separated on a Florisil column as described above. Samples were evaporated to 0.5 ml final volumes. Mirex was added as the internal standard, 106 pg μl^{-1}. Two blanks were also analyzed and results were blank corrected and surrogate recovery corrected.

3.3.6 Determining Breakthrough for the High Volume Air Samples

High volume breakthrough of POPs was calculated using the following equation (Peters et al. 2000):

$$B_{HV} = PUF_{back} / (PUF_{front} + PUF_{back}) \quad (3.1)$$

Where B_{HV} is high volume break through. PUF_{back} is the concentration of the POP on the back PUF (pg m^{-3}) and PUF_{front} is the concentration of POP on the front PUF (pg m^{-3}). B_{HV} values of 0.33 or greater are considered to represent significant breakthrough (Peters et al. 2000). Significant breakthrough occurs when 50% or more of the chemical burden is on the back puff. Of the six compounds studied in this report, HCB showed significant breakthrough, with a value of 0.47. Thus we anticipate our reported air concentrations for HCB are underestimates of actual concentrations.

3.3.7 Dissolved Organic Carbon (DOC)

Water was filtered through a precombusted Gelman AE glass fiber filter, acidified pH <2.0, and sparged with purified CO_2 free air. This removed any CO_2 in the sample, produced from carbonates and bicarbonates (inorganic fraction). The sample was then burned at 680°C and the resulting CO_2 was measured in a nondispersive infrared detector, using a Shimadzu TOC-5000A total organic carbon analyser and ASI-5000A autosampler.

3.3.8 Analysis of Water and Air Samples

Samples were injected into a HP 6890 gas chromatograph (GC) for analysis. The GC was equipped with a 30m x 0.25mm DB-5 column with He carrier at 31 cm s^{-1}, and a

^{63}Ni electron capture detector (ECD) with the temperature set at 350°C. One μL of each fraction was injected in the split mode, purge vent off for 30 seconds, using a Hewlett Packard (HP) 7863 series auto-sampler. The injector was set at 220°C and the detector at 350°C. The oven temperature was programmed as follows: 80°C for two minutes, ramping at 10°C min^{-1} to 100°C, and 40°C min^{-1} to 280°C and held for five minutes. Chromatographic data were collected and analyzed using HP Chemstation. A five-point calibration set was used to quantify the sample peaks, with mirex as the injection internal standard. All samples were blank corrected and volume corrected using the internal standard mirex. They were also recovery corrected using the field surrogates 1,3,5-TBB, 1,2,4,5-TTBB and δ-HCH.

3.3.9 Air-Water Gas Exchange

See air-water gas exchange section in chapter 1 of this thesis.

3.3.10 Henry's Law Constants

The Henry's law constant H is the ratio of a compound's abundance in the gas phase to that in the aqueous phase at equilibrium (Schwarzenbach et al. 1993). Henry's law constants for organic compounds are calculated experimentally by measuring air and water concentrations at equilibrium, in a closed system using pure water, with units of Pa m^3 mol^{-1} (Mackay 1991). Because this value changes with temperature, calculation of air-water exchange fluxes for each of the POPs examined required Henry's law constants to be temperature adjusted, assuming air temperature at the surface is equal to surface water

temperature. Henry's law constants for the chemicals studied were temperature adjusted using the equation of Hoff et al. (1998):

$$H(T) = H(Tr)\ EXP(m(1/Tr - 1/T)) \quad (3.2)$$

Where H(T) is the Henry's law constant at a given temperature, H(Tr) is the Henry's law constant of a chemical determined experimentally at a reference temperature and m is a constant. H(Tr) values and m values for α-HCH and γ-HCH were from Kucklick et al. (1991), values for HCB were from Ten Hulsher et al. (1992), dieldrin values were from Tateya et al. (1988) and values for α-endosulfan and β-endosulfan were from Rice et al. (1997).

3.3.11 Calculating Inputs and Outputs of POPs

Daily net inputs of POPs into the lakes, or outputs by volatilization, were calculated by multiplying average air-water fluxes by the surface area of the lake:

$$\text{Flux (ng m}^{-2}\text{ d}^{-1}\text{)} * L_A\ (m^2) = \text{inputs/outputs per day (ng d}^{-1}\text{)} \quad (3.3)$$

where L_A is lake area. To determine the total amount gained or lost from air-water gas exchange during the entire field season, daily inputs/outputs were multiplied by the number of days over which samples were taken using the equation:

$$\text{inputs/outputs (ng d}^{-1}\text{)} * \text{days} = \text{total amount over a given time (ng)} \quad (3.4)$$

Daily loss from outflow (O_D, ng d^{-1}) was determined using the equation:

$$S * T_{res}^{-1} = O_D \quad (3.5)$$

Where S is total storage in lake water (concentration x volume, ng), and T_{res} is the mean residence time of water in the lake (days).

3.4 Results and Discussion

3.4.1 Magnitude and Direction of Gas Exchange

Rates of air-water gas exchange, as calculated with equation 1.9, showed net deposition of α-HCH at Bow Lake (Fig. 3.1, 3.2) from May through August of 1998. Maximum deposition of α-HCH occurred in the spring when air and water temperatures were at their lowest (Fig. 3.1), favouring the partitioning of α-HCH into water. In 1999 there was a surge in water concentrations of α-HCH at Bow Lake (Table 3.1; Fig. 3.2), while air concentrations remained similar to 1998 levels (Table 3.2; Fig. 3.2). Water concentrations were occasionally over-saturated with respect to air concentrations causing a reversal in the direction of air-water gas exchange at Bow Lake, from net deposition in 1998 to net volatilization by 1999 (Table 3.3; Fig. 3.1, 3.2).

Air-water gas exchange of α-HCH, at Bow Lake, showed net deposition in 1998 but displayed both deposition and evaporation during the 1999 and 2000 field seasons (Fig 3.1). This indicated calculated air-water gas exchange of α-HCH was more sensitive to fluctuations in water concentrations (McConnell et al. 1993, 1996) than by surface water temperatures which regulate the Henry's law constants. Air concentrations of α-HCH in this region were fairly similar between years (Table 3.2; Fig. 3.2), suggesting changes in air-water gas exchange were driven mainly by changing water concentrations (Table 3.1). The only exception to this was on June 28th of 2000 when the air concentration of α-HCH was about 6 times higher than the norm. This resulted in a high calculated deposition rate of α-HCH on that day, 43 ng m^{-2} d^{-1} (Fig. 3.2).

The air-water gas exchange of α-HCH was depositional at Donald (1999), Kananaskis (2000) and Dixon Dam (2000) (Table 3.3). Air concentrations of α-HCH

were similar at all of the sites (Table 3.1, 3.2), suggesting that air-water fluxes of α-HCH were mainly influenced by concentrations in water.

In 1998, high air concentrations of γ-HCH at Bow Lake coupled with cold water temperatures in the spring resulted in the highest rates of absorption in May and early June, 38 ng m^2 d^{-1} and 37 ng m^2 d^{-1} respectively (Fig. 3.1, 3.3). Net air-water gas exchange of γ-HCH shifted towards equilibrium as the summer progressed because air concentrations decreased and water temperatures increased (Fig. 3.1, 3.3). The high air concentrations of γ-HCH early in the spring may be attributed to planting of treated canola seeds across the Canadian prairie provinces (Waite et al. In press). In 1999 high surface water concentrations of γ-HCH (Table 3.1) was the dominating factor causing high rates of volatilization (Table 3.3; Fig. 3.1, 3.3). Major declines in water concentrations of γ-HCH at Bow Lake in 2000 relative to 1999 concentrations, coupled with declining air concentrations (Table 3.1, 3.2), resulted in more moderate rates of volatilization during the ice-free season (Fig. 3.1, 3.3). Average air concentrations of γ-HCH decreased from 1998 through 2000 (Table 3.2). This coincided with continued decreased uses of lindane across North America (NAWQA 2001; NPUD 2001; PISU 2001; Mark Howard, U.S EPA, pers. comm.). The decreasing γ-HCH concentrations in air and rising concentrations in water from 1998-2000, caused a reversal in the air-water gas exchange at Bow Lake in 1999 (Fig. 3.1, 3.3).

The large water concentrations of both α-HCH and γ-HCH in 1999, compared to 1998 and 2000 (Table 3.1), are likely a result of a larger than normal winter snow pack measured at Bow Lake. Both particle bound and gas-phase HCHs are readily scavenged from the atmosphere by snow because these chemicals have relatively low Henry's law

constants (Atlas et al. 1988; Czuczwa et al. 1988). After being deposited, HCHs readily elute through snow pack and drain during snowmelt (Wania 1997). Wania et al. (1999) and MacDonald et al. (2000) showed spring pulses of α-HCH, γ-HCH and endosulfan that coincided with snowmelt and Blais et al. (2001a) calculated that snow pack was a major contributor of POPs to Bow Lake. Maximum snow pack depth was 460 mm water equivalent on March 30th of 1999 compared to only 257 mm water equivalent on March 30th, 1998. In 2000, the snow pack was smaller near the beginning of the sampling period (239 mm water equivalent on May 30th) compared to 1999 levels (329 mm water equivalent on May 30th) (Table 2.4). This coincided with average water concentrations of α-HCH and γ-HCH being greatest in 1999, compared with 1998 and 2000 (Table 3.1).

Donald Station (1999) and Kananaskis Lake (2000) showed net evaporation of γ-HCH (Table 3.3) and had average air concentrations (Table 3.2) that were similar to those at Bow Lake. The net air-water exchange of γ-HCH was also sensitive to fluctuations in water concentrations at these sites. Dixon Dam (2000) showed net deposition of γ-HCH in 2000, however this site was located in an agricultural region and the average air concentration (Table 3.2) was skewed because of one very high value (114 pg m^{-3}), that likely resulted from a nearby application of lindane.

Breakthrough of HCB in the PUF plugs was significant because of a predominance of HCB on the back PUF filter. As a consequence, air concentrations were likely underestimated relative to actual values. Therefore, rates of volatilization may be overestimated. Taking air samples for the more volatile POPs should be done over a 24-hour period. Calculated volatilization of HCB occurred during the 1998, 1999 and 2000 ice-free seasons at Bow Lake (Table 3.3; Fig. 3.1). Both air and water concentrations of

HCB increased successively from 1998 through 2000 at Bow Lake (Table 3.1,3.2), resulting in average fluxes that remained largely constant over the three years (Table 3.3). The one exception to this was a high concentration of HCB in Bow Lake (56 pg L^{-1}) observed on June 1st of 2000 that resulted in an evaporative flux of 27 ng m^{-2} d^{-1} (Fig. 3.1).

Donald Station, Kananaskis Lake and Dixon Dam also displayed net volatilizations of HCB from open waters (Table 3.3). HCB has a high Henry's law constant (131 Pa m^3 mol^{-1} at 25°C, Table 3.4) (Mackay et al. 1992, 1997). As a result, net air-water gas exchange of HCB favoured volatilization from these lakes. Net volatilization of HCB was recorded during the summer at Lake Baikal, Russia, despite it being a very cold and deep lake (McConnell et al. 1996). The vapor pressure of the subcooled liquid (P_L) at 25°C for HCB is above one Pascal (P_a) (Table 3.4) and therefore shows little tendency to condense at ambient temperatures (Wania and Mackay 1996).

Net volatilization of dieldrin, at Bow Lake, was 0.96 ±0.33, 2.5 ±2.0 and 2.2 ± 0.96 (ng m^2 d^{-1}) during the sampling seasons of 1998, 1999 and 2000, respectively (Table 3.3; Fig. 3.1). The higher volatilization of dieldrin in 1999 and 2000, compared with 1998, was attributed to water concentrations of dieldrin increasing while air concentrations remained constant (Table 3.1, 3.2).

Net volatilization of dieldrin also occurred at Donald Station (1999), Kananaskis Lake (2000) and Dixon Dam (2000) (Table 3.3), because air concentrations were low relative to their water concentrations (Table 3.1,3.2). Net air-water exchange of dieldrin generally favoured volatilization from open water because of its high Henry's law constant and relatively low air concentrations (Table 3.3, 3.4).

Overall, air-water gas exchange of the α-endosulfan isomer at Bow Lake showed net deposition from 1998-2000 (Table 3.3). Average air concentrations of α-endosulfan: (14 pg m^{-3} in 1998, 28 pg m^{-3} in 1999 and 26 pg m^{-3} in 2000, Table 3.2), were high enough to cause net deposition during the three years.

The average air-water flux of the β-endosulfan isomer was from water to air for the three summers at Bow Lake (Table 3.3), 1998-2000. A particularly large evaporation was calculated for July 25th, 2000 (Fig 3.1), when the water concentration surged to 53 pg L^{-1} while the air concentration was recorded at a low 0.1 pg m^{-3}. The result was a strong concentration gradient at the air-water interface, favouring high volatilization rates of β-endosulfan (Fig. 3.1).

Net deposition of α-endosulfan also occurred at Donald Station, Kananaskis Lake and Dixon Dam (Table 3.3). β-endosulfan showed net volatilization at Donald Station in 1999, while air-water gas exchange favoured deposition at Kananaskis and Dixon Dam in 2000 (Table 3.3). Net deposition of β-endosulfan at Kananaskis Lake and Dixon Dam was attributed to their higher air concentrations, relative to Bow Lake and Donald Station (Table 3.1, 3.2).

Technical endosulfan is made up of 7 parts α-endosulfan and 3 parts β-endosulfan (NRCC 1975). Average water concentrations of the two endosulfan isomers were similar (Table 3.1). Therefore, the opposing direction of air-water exchange (Table 3.3) was a result of the large differences in air concentrations (Table 3.2). At Bow Lake, α-endosulfan to β-endosulfan ratios in air were 40, 50 and 9.3 in 1998, 1999 and 2000 respectively. Rice et al. (1997) found α-endosulfan to β-endosulfan ratio in air was approximately 9:1, from samples taken directly after application of technical endosulfan

onto soil. Burgoyne and Hites (1993), considered α-endosulfan to be the only endosulfan isomer of significance in the atmosphere. Experiments have indicated that vapour phase β-endosulfan may convert to α-endosulfan (Rice et al. 1997). Also, atmospheric β-endosulfan is 5.7-fold more likely to be scavenged by rain owing to its lower Henry's law constant (Rice et al. 1997). This may account for the small amounts in air and the relatively higher amounts in water. As a consequence, the concentration gradient of β-endosulfan favoured volatilization, while that of α–endosulfan favoured deposition (Table 3.3; Fig. 3.1).

3.4.2 Relative Inputs/Outputs from Air-Water Gas Exchange

There are no direct anthropogenic emissions of POPs into this region of the Rocky Mountains. All contaminants found in these lakes ultimately came from atmospheric deposition, as a result of medium and long-range transport. We assume that inputs of POPs into the lakes arrived from inflow tributaries, overland runoff, aerosol deposition, precipitation and net deposition from air-water gas exchange. Likewise, we assume that losses occurred via outflow streams and rivers, sedimentation, degradation reactions and net volatilization from air-water gas exchange. Calculated sedimentation at Bow Lake, by Blais et al. (2001b) accounted for roughly 20% of α-HCH output and 37% for γ-HCH, with the remainder lost by outflow. The mass balance budget estimated that deposition of α-HCH and γ-HCH into Bow Lake, from air-water gas exchange, contributed 27% and 40% respectively of the total loadings. The mass balance for dieldrin output at Bow Lake was approximated 57% sedimentation, 23% outflow and 20% volatilization (Blais et al. 2001b).

Contributions of α-HCH from air-water gas exchange were variable from year to year at Bow Lake (Table 3.5), but overall air-water gas exchange of α-HCH was depositional. Net deposition across the air-water interface added 1.2 grams (7.5% of initial storage) into Bow Lake in 2000 and 3.8 grams (46% of initial storage) in 1998 (Table 3.5). Moderate gains of α-HCH from net deposition, was also seen at Kananaskis Lake and Dixon Dam (Table 3.5). Volatilization accounted for 3.9% of loss from initial storage at Bow Lake in 1999. The high water concentrations of α-HCH that year resulted in net volatilization. Overall, air-water gas exchange was a source of α-HCH to these lakes (Table 3.5).

Air-water exchanges of γ-HCH are highly variable from year to year, showing net deposition into lakes some years and net volatilization during other years (Table 3.5). Net deposition at Bow Lake in 1998 contributed 3.6 grams, or approximately 110% of the initial total storage, during the sampling period from May to August. However, γ-HCH volatilized from Bow Lake in 1999, with a calculated loss of 3.5 grams. Daily loss from volatilization in 1999 was about one fourth of the amount lost from outflow (Table 3.5). These results showed that air-water gas exchange acted as a source of γ-HCH to Bow Lake in 1998, and as a mechanism for removal of γ-HCH in 1999 and 2000.

Differences in the direction of γ-HCH flux were observed between sites. From May through August of 2000, 2.4 grams of γ-HCH were lost from volatilization at Kananaskis (22% of initial total storage) and represented about one third of the estimated outflow (Table 3.5). At Dixon Dam, γ-HCH displayed net deposition that contributed about 7 grams during the season, representing 11% of the initial storage.

The HCHs displayed both net gains and net losses from air-water gas exchange over time (Table 3.5). Therefore net air-water gas exchange of α-HCH and γ-HCH can either act as a source or a loss from these lakes (Table 3.5; Fig. 3.1), with air-water gas exchange being important to the overall lake inventory.

Volatilization accounted for substantial losses of HCB from all of the lakes studied (Table 3.5). Ratios of volatilization:outflow ranged from as high as 9.3 in 1998 at Bow Lake to as low as 0.12 at Kananaskis. It was estimated that volatilisation of HCB was the main output route at all of the lakes except for Kananaskis, where outflow may have been more significant (Table 3.5).

Dieldrin volatilized at all lakes except at Kananaskis, where net deposition from air-water gas exchange added 0.01 grams during the sampling season (1% of initial storage) (Table 3.5). Losses from volatilization exceeded losses from outflow at Bow Lake in 1998 and 2000, and at Dixon Dam in 2000. As a result, air-water gas exchange was viewed as an important pathway for net loss of dieldrin from these lakes. Both HCB and dieldrin are more likely to volatilize from water, compared to the HCHs and endosulfans, because of their higher Henry's law constants (Table 3.4).

Air-water gas exchange was a source of α-endosulfan to all of the sites studied. Total calculated gains to the lakes during the sampling season ranged from 19 grams at Dixon Dam to 45 grams at Kananaskis (Table 3.5). Total losses from the outflows during sample collection were approximately 6 grams at Dixon Dam and 0.5 grams at Kananaskis. Daily losses from the outflow were much smaller than gains from air-water gas exchange, suggesting outflow was not the main mechanism for loss (Table 3.5). Other possible losses include sedimentation, uptake by biological organisms, biological

degradation and chemical degradation. The half-life of endosulfan in water ranges from 5 weeks to 5 months (NRCC 1975; Howard et al. 1991). Using these half-lives, calculated degradation over the sampling season would account for a loss of 5.5 grams to 24 grams at Dixon Dam (-54 mg d^{-1} to -240 mg d^{-1}) and between 0.45 grams to 2.0 grams at Kananaskis (-4.6 mg d^{-1} to –20 mg d^{-1}). Loss of α-endosulfan from outflows, during the sampling period, was 6.0 grams at Dixon Dam and 0.48 grams at Kananaskis. Clearly degradation rates vary greatly and potentially account for a major portion of α-endosulfan loss from these lakes.

β-endosulfan displayed net volatilization from Bow Lake during the sampling seasons of 1998-2000. Ratios of volatilization:outflow were 0.56 in 1998 and 0.94 in 1999. This indicated that volatilization played an important role in the overall loss of β-endosulfan from Bow Lake. Net deposition of β-endosulfan occurred during the ice-free season in 2000 at Kananaskis Lake and Dixon Dam (Table 3.5). Air-water gas exchange contributed 1.9 grams of β-endosulfan into Kananaskis during the summer (160% of the initial storage). This represents a large input compared to the overall storage in the lake; indicating air-water gas exchange is likely an important source of β-endosulfan to this lake. Net deposition from air-water gas exchange at Dixon Dam contributed 1.3 grams during the sampling period (9.3% of the initial storage) (Table 3.5). The large difference in net deposition of β-endosulfan between the two lakes is explained by the higher air concentrations observed at Kananaskis (Table 3.2). Technical endosulfan is still used in North America (Rice et al. 1997) so the high water concentrations of α-endosulfan and β-endosulfan found in Dixon Dam during the spring may have been from local emissions

(Table 3.5). These emissions are possibly the dominant source of endosulfans to Dixon Dam.

Air-water gas exchange can be both an important source of POPs into lakes or an important pathway for the loss of POPs from lakes. These results showed that air-water gas exchange was an important loss for the compounds with higher Henry's law constants, such as HCB and dieldrin, from the study lakes in the spring and summer. Net deposition from air-water gas exchange in the spring and summer was an important contributor of α-endosulfan to these lakes. Net air water gas exchanges of the HCHs and β-endosulfan acted as either a source to the lakes or a loss from the lakes, because of their widely fluctuating water concentrations.

3.5 Conclusions

The direction and magnitude of air-water exchange of several POPs were determined for alpine, montane and prairie lakes in western Canada. Net air-water exchange of HCB and dieldrin were primarily from water to air, due in part to their high Henry's law constants. α-endosulfan displayed net deposition while β-endosulfan volatilized. The direction and magnitude of the air-water gas exchanges for the HCHs changed frequently during the three seasons at Bow Lake. Calculations showed that the magnitude and direction of air-water gas exchanges were not significantly correlated with site elevation or temperature. The results demonstrated air-water gas exchange was more sensitive to relative air and water concentrations, rather than temperatures. Concerning relative inputs and losses from air-water gas exchange, it was revealed that volatilization was a more significant loss for HCB than outflow. Net volatilisation was also an

important loss for dieldrin, with the exception of Kananaskis Lake. Gas absorption was seen as a significant source of α-endosulfan to the lakes studied. Net gas exchange of α-HCH, γ-HCH and β-endosulfan was found to be less significant to lake inventory, compared to the other compounds. Air-water gas exchange of POPs is mainly sensitive to the variable air and water concentrations, and less sensitive to variation in temperature.

Table 3.1 Averaged water concentrations (Standard Deviations in brackets) of selected organochlorines at four different locations ranging in altitude from 770 to 1975 masl. Sample collection spanned from May – August in 1998, June- August in 1999 and from May – August in 2000. All concentrations are in (pg L^{-1}). HCH is hexachlorocyclohexane and HCB is hexachlorobenzene.

Location and Date	**Elevation (masl)**	**α-HCH**	**γ-HCH**	**α-endosulfan**	**β-endosulfan**	**HCB**	**Dieldrin**
Bow Lake	1975						
1998		130 (46)	83 (34)	5.7 (1.7)	3.6 (0.5)	5.4 (1.5)	9.4 (3.1)
1999		470 (130)	410 (200)	15 (6.6)	18 (8.2)	19 (3.5)	16 (15)
2000		210 (43)	130 (24)	19 (15)	23 (18)	21 (17)	22 (5.0)
Kananaskis							
2000	1667	160 (31)	140 (29)	15 (7.9)	17 (9.4)	15 (5.0)	120 (3.5)
Dixon Dam							
2000	946	74 (13)	530 (150)	20 (20)	23 (23)	12 (6.4)	5.5 (3.4)
Donald							
1999	770	180 (61)	390 (340)	15 (16)	19 (20)	16 (6.7)	14 (19)

Table 3.2 Air concentrations, in pg m^{-3}, (Standard Deviations for each data set in brackets) of selected organochlorines taken at Bow Lake, Donald Station, Kananaskis Lake and Dixon Dam. Samples were taken with a high-volume air sampler (Anderson Inc.) spanning May –August in 1998, June-August in 1999 and May-August in 2000. Concurrent air temperatures were taken with a data logger every two hours. HCH is hexachlorocyclohexane and HCB is hexachlorobenzene.

Location and Date	**Elevation (masl)**	**α-HCH**	**γ-HCH**	**α-endosulfan**	**β-endosulfan**	**HCB**	**Dieldrin**
Bow Lake	1975						
1998		36 (7.8)	21 (20)	14 (8.3)	0.35 (0.27)	8.7 (4.4)	0.47 (0.34)
1999		36 (17)	8.1 (5.1)	28 (17)	0.56 (0.68)	17 (11)	0.77 (0.57)
2000		21 (25)	2.3 (1.6)	26 (8.9)	2.8 (2.3)	42 (12)	1.9 (1.2)
Kananaskis							
2000	1667	33 (39)	0.3 (0.4)	230 (230)	15 (21)	66 (77)	6.2 (5.3)
Dixon Dam							
2000	946	14 (13)	40 (69)	31 (25)	4.8 (5.2)	30 (14)	3.2 (3.2)
Donald							
1999	770	26 (11)	8.3 (7.9)	20 (20)	1.5 (3.1)	15 (7.8)	0.84 (1.2)

Table 3.3 Averaged air-water fluxes (ng m^{-2} d^{-1}) (Standard Deviations in brackets) of selected organochlorines at four different locations ranging in altitude from 770 to 1975 masl. Sample collection spanned from May – August in 1998, June- August in 1999 and from May – August in 2000. Positive numbers represent net deposition and negative numbers represent net volatilization in (ng m^{-2} d^{-1}). HCH is hexachlorocyclohexane, HCB is hexachlorobenzene.

Location and Date	Elevation (masl)	Mean air Temp.	Sampling Time	α-HCH	γ-HCH	α-endosulfan	β-endosulfan	HCB	Dieldrin
Bow Lake	1975								
1998		10.4	99 days	14 (6.1)	13 (17)	7.2 (4.4)	-0.22 (0.25)	-5.0 (1.8)	-0.96 (0.33)
1999		8.2 ± 4.9	69 days	-6.8 (16)	-18 (16)	18 (14)	-2.1 (1.5)	-3.2 (0.74)	-2.5 (2.0)
2000		8.4 ± 5.0	113 days	3.9 (22)	-3.0 (2.5)	9.4 (6.1)	-1.4 (2.6)	-7.0 (11)	-2.2 (0.96)
Average				3.7 (10)	-2.7 (15)	12 (5.7)	-1.2 (0.95)	-5.1 (1.9)	-1.9 (0.82)
Kananaskis 2000	1667	9.6 ± 6.2	98 days	5.5 (19)	-4.6 (2.5)	88 (98)	3.6 (8.3)	-0.1 (5.8)	0.027 (2.3)
Dixon Dam 2000	946	12.3 ± 5.4	102 days	2.0 (5.5)	3.7 (32)	10 (8.2)	0.75 (1.8)	-2.3 (0.68)	-0.73 (0.44)
Donald 1999	770	14.1 ± 4.3	63 days	0.36 (18)	-28 (38)	14 (17)	-0.88 (3.5)	-2.8 (1.1)	-1.9 (3.2)

Table 3.4 Physical and chemical properties of selected persistent organic pollutants. Data are from Mackay et al. (1992; 1997) and Rice et al. (1997). Henry's law constants and vapour pressures are calculated for 25°C.

Chemical Compound	Water Solubility ($g\ m^{-3}$) 25°C	Henry's Law Constant ($P_a\ m^3\ mol^{-1}$), at 25°C	Subcooled pressure (P_L, P_a)	Sorption coefficient Log K_{oc}	Log K_{ow}
α-HCH	1.0	0.87	0.1	3.8	3.8
γ-HCH	7.3	0.15	0.027	3.0	3.7
α-endosulfan	0.5	6.6	0.008	3.4	3.6
β-endosulfan	0.45	0.88	0.39	3.5	3.8
HCB	0.005	130	0.25	5.2	5.5
Dieldrin	0.17	1.1	0.016	4.1	5.2

Table 3.5 Initial amounts (day 1 of the sample season) and final amounts (last day of the sample season) are whole lake inventories estimated by multiplying concentrations by lake volume. Total change in amount is the difference between the estimated initial amount and estimated final amount. Daily amounts gained or lost from air-water gas exchange were calculated by multiplying fluxes by the area of the lake. Total gain/loss from air-water gas exchange was calculated by multiplying daily gain/loss by the number of days over which the site was sampled. Loss per day from outflow was calculated by multiplying the estimated total storage by 1/mean residence time (days).

Location and Date	Compound	Initial Amount (grams)	Final Amount (grams)	Total Change (grams)	Total Gain/loss from air-water gas exchange (grams)	Loss per day from outflow (mg d^{-1})	Daily gain/loss from air-water gas exchange (mg d^{-1})
Bow (1998) May -August	α-HCH	8.2	6.3	-1.9	+3.8	-40	39
	γ-HCH	3.3	3.6	+0.25	+3.6	-16	36
	HCB	0.3	0.19	-0.1	-1.4	-1.5	-14
	Dieldrin	0.47	0.35	-0.09	-0.27	-2.3	-2.7
	α-endosulfan	0.34	0.20	-0.14	+2.0	-1.7	20
	β-endosulfan	0.22	0.20	0.02	-0.061	-1.1	-0.62
Bow (1999) June 4th - August 15th	α-HCH	33	17	-15	-1.3	-160	-19
	γ-HCH	41	9.2	-32	-3.5	-200	-50
	HCB	1.3	1.3	-0.03	-0.61	-6.3	-9.0
	Dieldrin	2.1	0.8	-1.4	-0.48	-10	-7.0
	α-endosulfan	1.1	1.2	+0.1	+3.6	-5.4	50
	β-endosulfan	1.3	1.5	+0.17	-0.41	-6.3	-5.9
Bow (2000) April 25th - August 15th	α-HCH	16	11	-4.9	+1.2	-78	11
	γ-HCH	8.7	5.8	-2.9	-0.7	-42	-8.4
	HCB	0.88	1.1	+0.2	-2.2	-4.3	-20
	Dieldrin	1.2	1.4	+0.17	-0.69	-5.9	-6.2
	α-endosulfan	0.57	1.6	+1.0	+3.0	-2.8	26
	β-endosulfan	1.2	1.4	+0.17	-0.45	-5.9	-3.9
Kananaskis (2000) May 2nd - August 7th	α-HCH	13	11	-2.0	+2.9	-63	29
	γ-HCH	11	8.6	-2.9	-2.4	-54	-24
	HCB	0.95	0.95	0	-0.05	-4.6	-0.53
	Dieldrin	0.92	0.85	0.07	+0.01	-4.5	0.14
	α-endosulfan	1.0	0.66	-0.34	+45	-4.9	460
	β-endosulfan	1.2	0.78	-0.44	+1.9	-5.9	19
Dixon Dam (2000) April 22nd - August 1st	α-HCH	16	16	-0.08	+3.6	-78	35
	γ-HCH	58	98	40	+6.6	-280	65
	HCB	2.1	1.7	0.35	-4.1	-10	-40
	Dieldrin	0.68	1.9	+1.2	-1.3	-3.3	-13
	α-endosulfan	12	1.3	-11	+19	-59	180
	β-endosulfan	14	1.5	-13	+1.3	-68	13

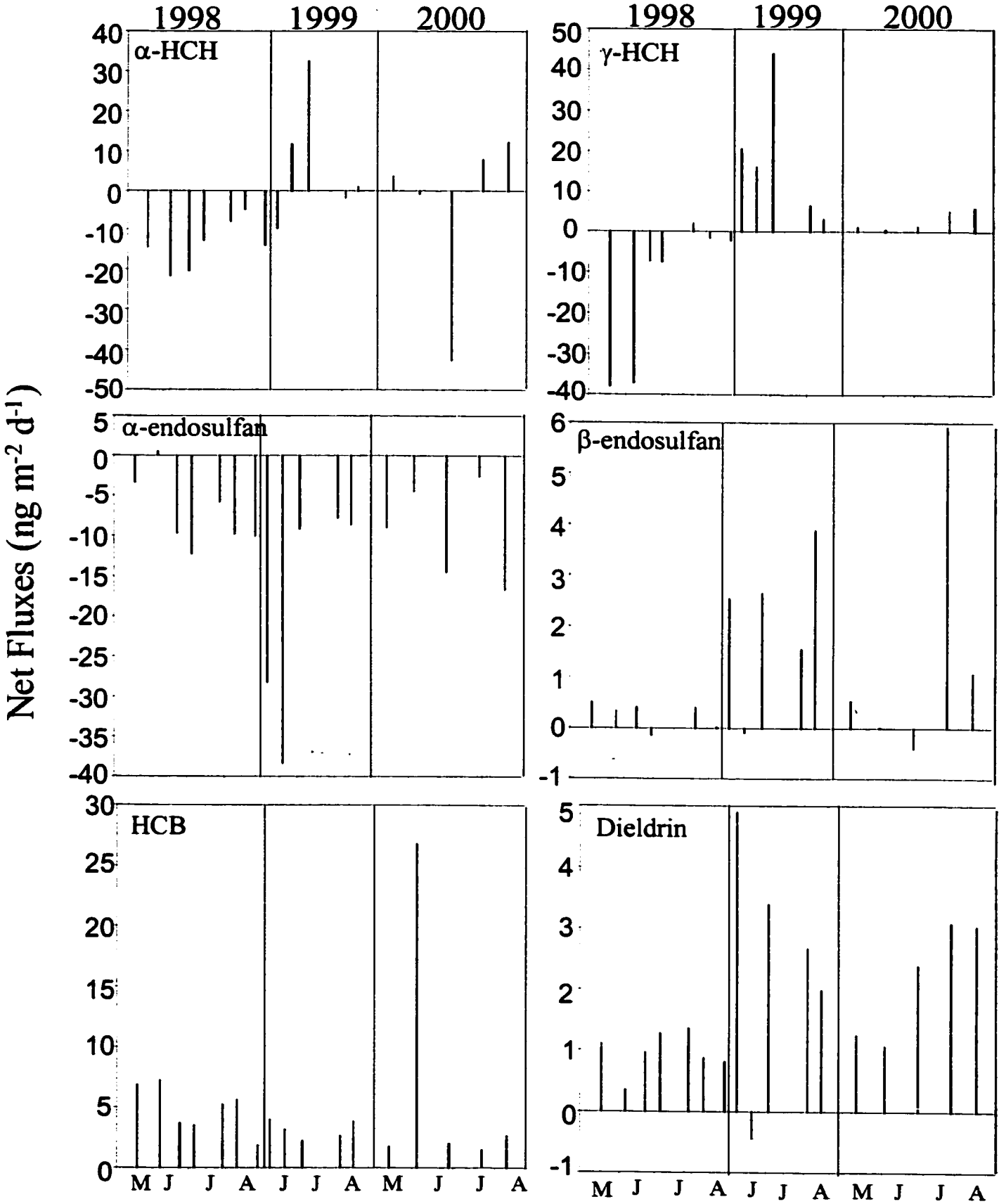

Figure 3.1 Net air-water gas exchange fluxes of α-hexachlorocyclohexane, γ-hexachlorcyclohexane α-endosulfan, β-endosulfan, hexachlorobenzene and dieldrin at Bow Lake. Fluxes were calculated during the ice-free seasons of 1998, 1999 and 2000.

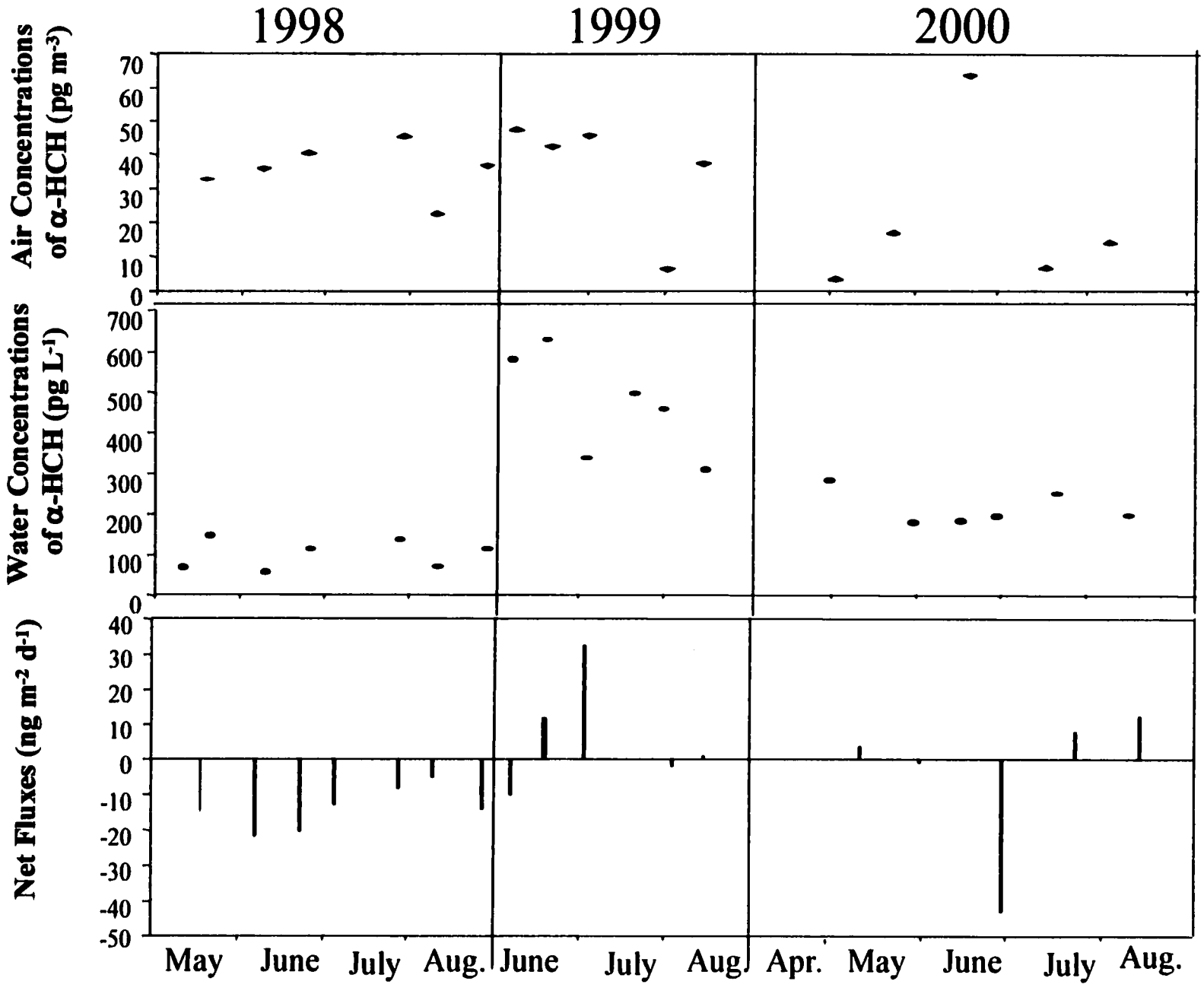

Figure 3.2 Air and water concentrations and air-water gas exchange of α-HCH at Bow Lake, calculated during the spring and summer of 1998-2000.

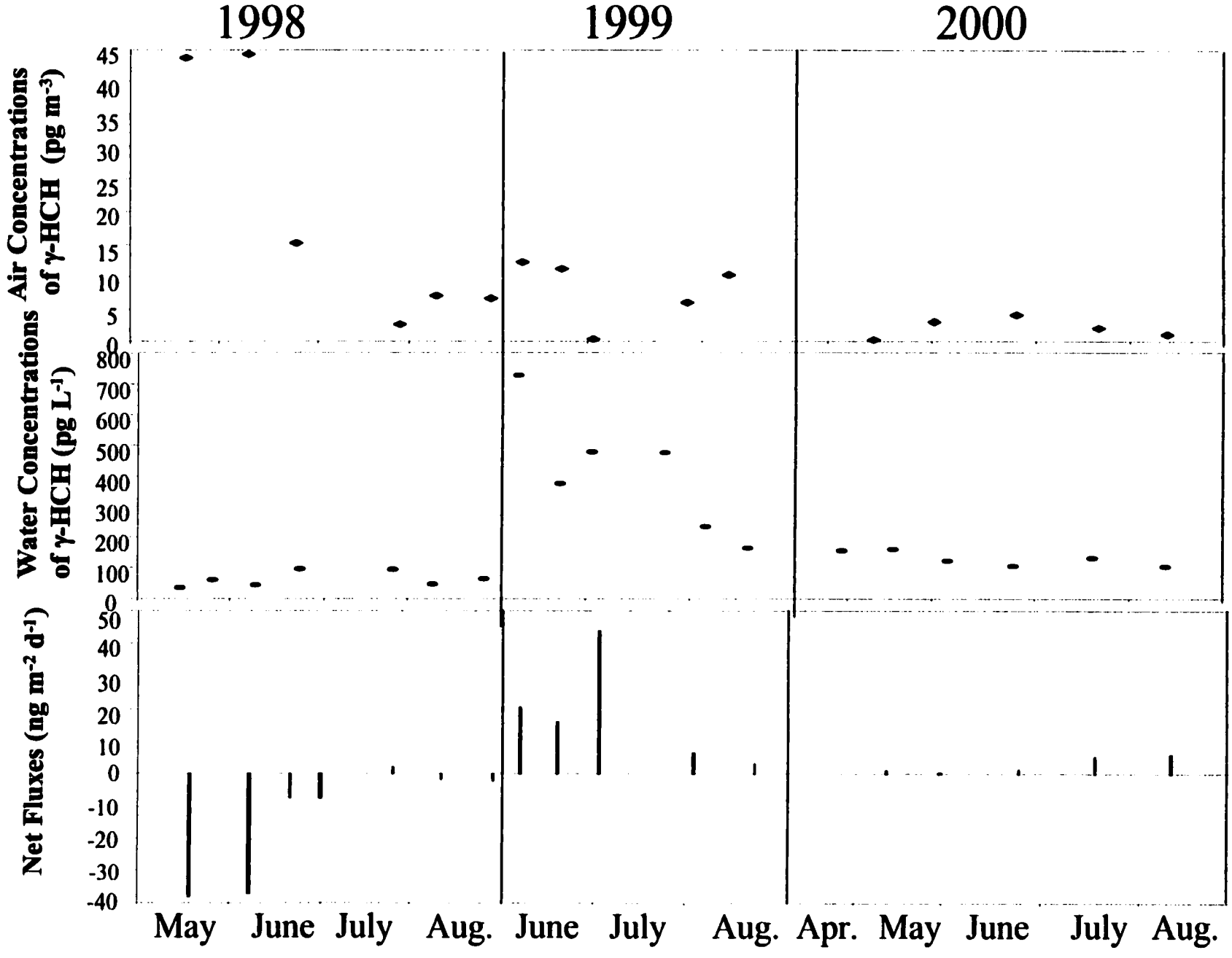

Figure 3.3 Air and water concentrations and air-water gas exchange of γ-HCH at Bow Lake, calculated during the spring and summer of 1998-2000.

4.0 General Discussion

The global distribution of chlorinated POPs by long range atmospheric transport has been a concern for several decades (George and Frear 1966; Rappe 1975; Goldberg 1975; Barrie 1986). Environmental organochlorines are persistent, they bioaccumulate and they are hazardous to wildlife and humans (Muir et al. 1988; Norstrom et al. 1988; Thomann et al. 1989; Erickson 1997), hence many POPs have been banned in developed countries.

The accumulation of several POPs in arctic and sub-arctic lakes and oceans has been well documented (Muir et al. 1988; Jantunen and Bidleman 1993; Falconer et al. 1995), with some of the more volatile POPs found at higher concentrations compared to warmer source regions (Jantunen and Bidleman 1996, 1998; Wania and Mackay 1996). Accumulation of POPs has also been observed at high altitudes in mountainous regions (Blais et al. 1998; Donald et al. 1999; Grimalt et al. 2001). Blais et al. (1998) found organochlorine deposition in snow increased between 10 to 100 fold between 770 and 3 100 meters in altitude. In high mountain lakes of Europe, Grimalt et al. (2001) observed an increase in the less volatile organochlorine compounds in fishes and sediments with increasing elevation. These results fit well with the global distillation model developed by Wania and Mackay (1993, 1996). However, accumulation patterns of POPs in mountain lakes are not well documented.

This study was undertaken to examine distillation patterns of POPs in mountain lakes and to examine partitioning of POPs between air and water. The more volatile POPs did not increase in concentration in the lakes as a function of elevation, despite cooler temperatures at higher elevations (Chapter 2, this thesis). This was in contrast to my original hypothesis that the more volatile POPs would increase with elevation, as

predicted by the global distillation model (Wania and Mackay 1993, 1996). A significant correlation between water concentrations and altitude was seen for heptachlor epoxide in 1999 ($p = 0.03$) and dieldrin in 2000 ($p = 0.024$), but these trends were not reproduced in other years. There are several reasons why distillation of POPs with elevation, due to cold condensation, was not observed. Temperatures during the summer months may not have been cold enough to cause significant deposition of the more volatile POPs. As well, differences between the lakes were not accounted in our original model. There were large differences in lake size and volume (Table 1.1), and hence differences in relative retention times. In addition, Dixon Dam Lake and Vermilion Lake were eutrophic while others were oligotrophic, and lakes located at higher elevations may have been exposed to air masses from more distant sources.

Air concentrations of POPs were not correlated with temperature, possibly because air masses were arriving from different sources at the different locations. Haugen et al. (1998) showed that concentrations of α-HCH in air were largely dependent on the origin of the air mass and not on temperature, in southern Lista, Norway. This was attributed to the fact that α-HCH was arriving from long-range transport and not revolatilizing from local sources. It has been suggested that air concentrations of POPs only show temperature dependence near emission sources or in contaminated areas, due to local revolatilization (Haugen et al. 1998; Wania et al. 1998). Temperature dependence of atmospheric POPs in regions that are contaminated by long-range transport, like the arctic, is not observed because concentrations are dominated by the inflow of air (Wania et al. 1998).

Observations revealed that water concentrations of POPs with a relatively lower K_{ow} peaked in the spring, coinciding with snowmelt (Chapter 2, this thesis). Elevated water concentrations of several POPs coinciding with snowmelt have been well documented (Semkin 1996; Barrie et al. 1997; Wania et al. 1999; Blais et al. 2001b). At Bow Lake it was observed that concentrations of many POPs were elevated in 1999, a high snowfall year. In the Canadian Rockies these compounds accumulate in snow pack over winter because of high precipitation rates (Blais et al. 2001a), cold temperatures and decreased rates of photochemical and biological degradation. The more water soluble POPs are then transported to the lakes with snowmelt, via inflows (Wania 1997, 1999; Chapter 2, this thesis).

Net air-water gas exchange of POPs across the air-water interface was examined at four lakes spanning an altitude of 1205 meters (Chapter 3, this thesis). Calculated results showed there was no correlation with magnitude and direction of gas exchange and temperature. As a consequence, the magnitude and direction of air-water gas exchange was not correlated with lake elevation or Julian day. However, organochlorine compounds with a lower Henry's law constant were more susceptible to net deposition and conversely POPs with a higher Henry's law constant were more susceptible to net volatilization. Similar results were found by McConnell et al. (1996), who showed net deposition of OCs with lower Henry's law constants, like α-HCH and γ-HCH. Likewise, their results also displayed net volatilization of compounds with higher Henry's law constants like HCB and the lower chlorinated PCBs, at Lake Baikal.

The magnitude and direction of gas flux was more sensitive to relative air and water concentrations of POPs compared to the chemical's Henry's law constant (Chapter

3, this thesis). Jantunen and Bidleman (1995) demonstrated the importance of relative air and water concentrations regulating air-water gas exchange of HCHs in the Bering and Chukchi Seas. They found a reversal in the air-water gas exchange direction of hexachlorocyclohexanes, from net deposition in 1988 to net volatilization in 1993. This was attributed to air concentrations declining faster than water concentrations after Russia and India banned and restricted technical HCH in 1990 (Li et al. 1998; Willett et al. 1998). As a result, the water-air fugacity ratios increased resulting in a reversal from net deposition in 1998 to net volatilization in 1993.

When comparing the major inputs and losses of POPs to these lakes air-water gas exchange was found to be an important factor regulating total concentrations of HCB, dieldrin, endosulfans and to a lesser extent α and γ-HCH, during the ice-free season (Chapter 3, this thesis). Ridal et al. (1996), observed that air-water gas exchange was probably a major factor moderating HCH concentrations in Lake Ontario, and Totten et al. (2001) observed net volatilization was important for removing tri- and tetrachlorobiphenyls from the New York-New Jersey Harbor during the summer months. Blais et al. (2001b) did a more accurate pollutant budget of POPs at Bow Lake which included inflow, wet deposition, outflow, sedimentation, change in storage and air-water gas exchange. Their results found that calculated volatilization of dieldrin accounted for 20% of its loss from Bow Lake. Calculated air-water gas exchange of α-HCH and γ-HCH showed that net deposition contributed approximately 27% and 40% respectively, of total loadings to Bow Lake.

It was predicted that net air-water gas exchange at these lakes would be an important removal process for compounds with high Henry's law constants and an

important source for compounds with lower Henry's law constants (Chapter 3, this thesis). This prediction was found to be true for HCB, α-endosulfan and dieldrin, because they had a high Henry's law constant and displayed high rates of volatilization. Likewise, the HCHs have lower Henry's law constants and they displayed relatively lower rates of volatilization. However, flux direction was inconsistent for α-HCH, γ-HCH and β-endosulfan. In general, the direction of air-water gas exchange can not be predicted by a chemicals Henry's law constant alone, because the flux direction is more sensitive to relative air and water concentrations.

For a more accurate estimate of the average air-water gas exchanges, it would be of interest to take weekly or bi-weekly air and water samples at these lakes. These estimates are only as reliable as the corresponding data measurements. Ridal et al. (1996) estimated a propagation of error in seasonally averaged net fluxes, calculated from weekly samples taken from May to October 1993, that had an uncertainty of ±75%.

In conclusion, environmental POPs with subcooled liquid vapour pressures between 0.001 Pa and 1.0 Pa were measured in Rocky Mountain lakes spanning an elevation of 1430 meters. The elevated concentrations of POPs found in these remote lakes located in National and Provincial Parks can only be explained by long-range transport. Temperature was not correlated with either water concentrations or air concentrations of POPs. Maximum water concentrations of HCHs were observed during the spring, coinciding with snowmelt. This indicated snowmelt was an important contributor of organochlorine compounds with a lower K_{ow}, to these lakes. Calculated air-water gas exchanges did not correlate with temperature. Chemicals vary in their tendencies to partition into air or water, as measured by their Henry's law constants, but

ultimately it is the fugacity gradient set up by relative air and water concentrations that determine magnitude and direction of air-water gas exchange. Collectively, the results indicate that distribution of POPs throughout the Canadian Rocky Mountains is highly influenced by precipitation levels. Results show a strong link between contaminant cycling and the hydrological cycle.

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Appendix 1. Water concentrations of selected POPs in selected lakes of the Canadian Rocky Mountains. Water temperatures were taken at the time of sampling. All concentrations are in pg L^{-1}.

Location and Date	Water Temperature at Time of Sampling	α-HCH	γ-HCH	HCB	Heptachlor Epoxide	Dieldrin	α-endosulfan	β-endosulfan	*Sum of 130 PCB Congeners	pp-DDE	pp-DDD	op-DDT
Bow Outflow												
June 6, 97	N/A	118	61.6	3.5	1.2	17.2	4.5	10.0	N/A	0.0	0.0	0.0
June 20, 97	N/A	113	46.1	3.0	1.6	4.5	3.5	7.7	N/A	0.0	0.0	0.0
July 1, 97	N/A	87.5	43.0	5.1	2.9	9.7	4.2	15.7	N/A	0.9	2.0	0.13
July 13, 97	N/A	112	44.5	4.4	3.4	6.7	5.5	11.6	N/A	1.9	2.5	0.051
July 29, 97	N/A	253	874	8.8	6.1	23.1	14.6	36.1	N/A	0.44	1.1	0.0
Aug. 10, 97	N/A	113	42.9	2.7	2.5	8.3	7.8	28.3	N/A	0.79	4.8	0.15
Aug. 24, 97	N/A	198	71.4	4.4	5.0	12.0	11.7	29.3	N/A	20.2	2.5	2.1
Averages		142	169	4.6	3.2	11.6	7.4	19.8	N/A	3.5	1.8	0.30
SD		59.9	311	2.1	1.8	6.5	4.2	11.2	N/A	7.4	1.7	0.80
Bow Outflow												
May 10, 98	6.5	69.4	35.2	4.3	1.8	8.9	7.2	3.0	793	0.36	1.6	0.0
May 20, 98	7.7	147	59.7	5.3	2.5	8.3	6.0	4.0	290	0.0	3.5	0.0
June 8, 98	9.6	56.5	43.5	2.8	2.1	4.3	4.0	3.0	113	0.0	17	0.0
June 24, 98	12.7	113	95.3	3.1	3.5	6.8	0.0	4.0	116	0.0	10.5	0.0
July 26, 98	15.4	139	94.0	4.8	3.9	8.5	7.7	0.0	146	0.0	13.2	0.0
Aug. 9, 98	14.3	70.3	46.1	4.9	3.0	5.2	5.7	3.8	226	0.79	2.1	1.2
Aug. 26, 98	10.0	113	64.2	3.4	3.4	6.7	3.5	3.5	150	0.96	2.2	4.4
Averages	10.9	132	83.0	5.4	3.8	9.4	5.7	3.6	308	0.30	7.2	0.8
SD	3.4	46.4	34.4	1.5	1.0	3.1	1.7	0.5	314	0.42	6.3	1.6
Bow Outflow												
June 4, 99	1.8	581	728	23.2	24.0	37.3	19.7	23.4	220	0.0	4.4	0.0
June 16, 99	7.9	631	376	20.6	24.1	0.0	0.0	0.0	64.5	4.1	8.0	0.0
June 30, 99	9.5	338	479	16.3	12.5	23.9	20.4	24.2	66.8	6.7	4.5	0.0
July 17, 99	9.0	499	477	16.0	21.3	0.0	3.8	4.5	93.6	1.7	8.8	0.0
July 31, 99	9.0	459	235	15.7	12.2	19.7	11.7	13.9	147	N/A	3.7	0.0
Aug. 11, 99	13.9	309	164	22.7	11.1	12.6	20.8	26.4	153	5.5	4.4	0.0
Averages	8.5	470	410	19.1	17.5	15.6	15.3	18.5	124	3.6	5.9	0.0
SD	3.9	128	201	3.5	6.2	14.5	6.6	8.2	60.5	2.7	2.2	0.0

Appendix 1 (continued).

Location and Date	Water Temperature at Time of Sampling	α-HCH	γ-HCH	HCB	Heptachlor Epoxide	Dieldrin	α-endosulfan	β-endosulfan	*Sum of 130 PCB Congeners	pp-DDE	pp-DDD	op-DDT
Bow Outflow												
April 25, 00	0.4	283	155	15.7	0.0	21.6	10.2	12.1	100	2.4	6.5	0.0
May 30, 00	3.1	177	159	56.0	17.5	28.4	6.3	7.5	141	12.4	0.0	0.0
June 13, 00	3.5	183	123	10.8	8.7	13.6	12.3	14.6	69.9	2.5	2.5	0.0
June 28, 00	9.0	194	106	15.5	8.9	20.0	12.2	14.5	59.8	2.6	10.6	0.0
July 27, 00	10.5	251	132	11.4	0.0	22.2	45.1	53.5	82.4	3.6	8.3	0.0
Aug. 15, 00	9.2	196	105	19.2	10.1	24.7	28.3	33.6	110	7.2	16	0.0
Averages	6.0	214	130	21.4	7.5	21.8	19.0	22.6	93.9	5.1	7.3	0.0
SD	4.1	42.8	23.5	17.2	6.7	5.0	14.8	17.6	29.6	4.0	5.7	0.0
Bow Glacier												
June 7, 97	3.0	430	281	10.1	13.7	42.4	52.4	38.8	N/A	0.53	0.0	0.0
June 19, 97	2.9	254	148	4.8	7.7	23.3	18.1	16.7	N/A	0.0	0.0	0.0
June 30, 97	5.0	143	76.7	5.2	9.0	20.7	8.5	14.9	N/A	0.82	2.5	0.0
July 14, 97	5.4	195	93.2	6.3	8.0	21.3	15.9	25.8	N/A	1.7	5.6	0.20
July 28, 97	7.0	206	88.7	6.9	8.6	23.9	14.1	23.2	N/A	0.97	3.7	0.31
Aug. 11, 97	6.4	117	39.3	2.6	4.2	9.4	8.0	21.6	N/A	1.2	1.5	0.0
Aug. 25, 97	5.9	220	70.0	4.2	5.9	14.7	16.5	33.7	N/A	1.1	5.7	0.0
Averages	5.1	224	114	5.7	8.2	22.2	19.1	25.0	N/A	0.9	2.7	0.073
SD	1.6	102	80.6	2.4	3.0	10.3	15.2	8.7	N/A	0.54	2.4	0.13
Bow Glacier												
May 9, 98	2.5	115	99.2	8.3	6.9	23.9	38.0	20.0	810	5.9	2.0	2.3
May 18, 98	4.1	N/A	N/A	6.2	N/A	13.2	7.8	10.5	343	2.2	1.0	2.8
June 7, 98	5.7	136	159	7.7	8.6	18.3	0.0	8.0	802	0.0	12.5	0.0
June 23, 98	6.6	158	155	4.2	9.2	17.9	0.0	7.0	161	0.48	12.5	0.0
July 26, 98	7.2	206	98.7	5.9	7.6	13.1	7.3	5.7	124	0.14	31.1	0.92
Aug. 9, 98	6.8	208	101	0.5	6.8	14.3	7.3	8.6	13.2	0.0	29	0.0
Aug. 26, 98	6.4	195	66.8	6.6	4.6	10.2	21.4	9.3	300	0.0	24.1	0.0
Averages	5.6	229	151	7.3	9.8	22.4	16.4	9.9	464	1.2	16	0.86
SD	1.7	106	55.2	4.6	3.6	11.9	13.5	4.7	364	2.2	12.3	1.2

Appendix 1 (continued).

Location and Date	Water Temperature at Time of Sampling	α-HCH	γ-HCH	HCB	Heptachlor Epoxide	Dieldrin	α-endosulfan	β-endosulfan	*Sum of 130 PCB Congeners	pp-DDE	pp-DDD	op-DDT
Bow Glacial												
June 5, 99	2.5	427	302	23.5	34.7	67.9	92.6	110	75.7	3.5	3.9	0.0
June 18, 99	3.8	323	266	17.7	15.7	0.0	0.0	0.0	173	0.0	8.0	0.0
July 1, 99	4.7	311	125	19.1	15.1	50.1	31.8	37.8	120	3.3	12	0.0
July 15, 99	2.5	424	474	63.7	28.4	53.7	39.0	49.4	189	0.0	10.9	0.0
July 29, 99	5.7	527	237	13.9	19.5	40.9	35.8	42.5	119	3.1	6.8	0.0
Averages	3.8	403	281	27.6	22.7	42.5	49.8	59.9	135	2.0	8.3	0.0
SD	1.4	88.4	127	20.5	8.6	25.7	28.7	33.7	45.8	1.8	3.2	0.0
Bow Glacial												
April 24, 00	0.8	24.3	235	15.5	7.3	11.5	20.0	23.7	127	4.3	0.0	0.0
May 11, 00	3.5	15.6	118	18.2	6.5	17.8	7.6	8.9	118	0.0	2.9	0.0
June 1, 00	0.8	46.4	40.6	13.5	9.8	19.8	9.6	11.4	62.2	2.6	4.8	8.8
June 15, 00	5.0	116	60.7	18.4	12.3	23.8	23.5	27.8	63.2	8.3	0.0	13.4
June 28, 00	7.8	153	86.7	14.5	12.3	18.9	22.8	27.1	86.7	4.0	4.3	0.0
July 25, 00	4.4	331	157	16.0	21.6	37.3	136	162	171	9.9	16.5	0.0
Aug. 17, 00	9.0	295	124	16.3	23.4	50.2	53.2	63.2	163	0.0	0.0	0.0
Averages	4.5	140	118	16.1	13.3	25.6	39.0	46.3	113	4.2	4.1	3.2
SD	3.2	129	65.3	1.8	6.7	13.4	42.1	49.9	44.5	3.8	5.9	5.6
Rock Isle												
July 2, 99	0.9	496	602	25.3	22.0	40.4	298	377	250	0.0	0.0	0.0
July 8, 99	1.7	416	444	23.3	30.1	5.9	5.6	7.1	191	3.3	3.8	0.0
July 23, 99	10	272	257	17.5	18.8	17.6	6.8	8.6	250	0.0	8.6	0.0
Aug. 8, 99	12.8	295	260	14.7	17.7	7.5	0.0	0.0	46.4	0.0	6.4	0.0
Aug. 18, 99	12	223	174	8.2	10.1	11.5	3.6	4.6	166	1.2	3.2	0.0
Averages	7.5	340	348	17.8	19.7	16.6	62.9	79.5	181	0.9	4.4	0.0
SD	5.7	112	173	6.9	7.3	14.1	132	167	83.7	1.4	3.3	0.0

Appendix 1 (continued).

Location and Date	Water Temperature at Time of Sampling	α-HCH	γ-HCH	HCB	Heptachlor Epoxide	Dieldrin	α-endosulfan	β-endosulfan	*Sum of 130 PCB Congeners	pp-DDE	pp-DDD	op-DDT
Rock Isle												
June 17, 00	0.2	441	376	16.7	20.1	22.4	228	270	56.9	3.0	9.8	0.0
June 29, 00	2.3	480	271	25.2	12.6	19.3	102	121	147	0.0	15.2	0.0
July 27, 00	12.8	176	109	9.3	7.3	10.6	55.8	66.3	111	4.3	5.3	15.5
Aug. 16, 00	13	185	126	15.6	8.7	18.2	21.5	25.5	116	5.9	17.3	0.0
Averages	7.1	320	220	16.7	12.2	17.6	102	121	108	3.3	11.9	3.9
SD	6.8	163	127	6.5	5.7	5.0	90.2	107	37.4	2.5	5.4	7.8
Wapta												
June 5, 99	6.3	91.8	2730	31.0	4.2	11.0	31.7	37.6	176	0.0	0.0	0.0
June 16, 99	7.2	74.1	228	14.5	10.1	18.1	39.2	46.5	88.3	17	0.0	0.0
June 30, 99	7.5	133	302	18.1	7.2	12.0	21.1	25.1	112	0.0	0.0	0.0
July 14, 99	7.0	107	284	17.3	11.4	14.0	27.2	32.3	155	4.3	0.0	0.0
July 30, 99	8.3	65.6	80.5	14.8	12.4	4.5	2.4	3.0	161	0.0	0.0	0.0
Aug. 11, 99	10.5	58.1	22.1	14.9	8.7	18.3	27.3	34.5	314	6.6	2.1	0.0
Averages	7.8	88.3	608	18.4	9.0	13.0	24.8	29.8	168	4.7	0.35	0.0
SD	1.5	28.3	105	6.3	3.0	5.1	12.5	14.9	79.0	6.7	0.86	0.0
Wapta												
April 19, 00	0.7	30.2	207	16.4	4.4	0.0	23.1	27.5	119	0.0	0.0	0.0
May 3, 00	2.1	108	105	12.6	3.1	5.8	37.2	44.1	67.1	8.3	2.4	0.0
May 16, 00	5.2	30.2	63.3	39.5	1.8	1.7	16.9	20.1	114	0.0	6.0	0.0
June 7, 00	7.5	36.3	53.2	9.1	3.8	6.9	11.2	13.3	69.6	0.0	0.0	0.0
June 22, 00	7.0	25.7	22.0	10.5	5.1	8.7	12.2	14.5	104	2.2	3.6	3.3
July 13, 00	7.2	33.2	30.7	18.8	4.8	18.6	24.4	29.0	103	5.1	4.5	0.0
Aug. 8, 00	8.5	47.7	31.4	11.1	10.0	13.2	19.3	22.9	102	7.0	5.9	0.0
Averages	5.5	44.4	73.1	16.9	4.7	7.8	20.6	24.5	97.1	3.2	3.2	0.47
SD	3.0	28.8	65.1	10.6	2.6	6.4	8.9	10.5	20.6	3.6	2.5	1.2

Appendix 1 (continued).

Location and Date	Water Temperature at Time of Sampling	α-HCH	γ-HCH	HCB	Heptachlor Epoxide	Dieldrin	α-endosulfan	β-endosulfan	*Sum of 130 PCB Congeners	pp-DDE	pp-DDD	op-DDT
Vermilion												
June 11, 99	12.0	411	871	15.5	9.4	34.2	0.0	0.0	139	25.0	124	0.0
June 23, 99	12.2	421	883	17.0	10.2	0.0	0.0	0.0	265	18.0	65.1	0.0
July 7, 99	13.0	423	606	18.0	11.4	1.6	1.7	2.2	77.2	17.2	58.4	0.0
July 20, 99	17.0	376	551	12.8	9.4	17.9	0.0	0.0	287	14.1	60.3	0.0
Aug. 3, 99	23.9	380	283	11.5	7.7	3.3	0.0	0.0	59.6	20.7	72.6	0.0
Aug. 19, 99	20.3	188	146	5.8	5.0	0.0	0.0	0.0	119	8.3	41.1	0.0
Averages	16.4	366	557	13.4	8.9	9.5	0.3	0.4	158	17.2	70.3	0.0
SD	4.9	89.6	300	4.5	2.2	13.9	0.7	0.9	96.2	5.7	28.3	0.0
Vermilion												
April 18, 00	10.0	299	553	10.2	7.2	0.0	70.1	83.2	203	9.3	31.2	0.0
May 4, 00	10.4	165	58.9	9.0	0.0	0.0	35.8	42.5	162	7.8	121	0.0
May 17, 00	12.8	162	388	10.0	2.3	2.5	18.9	22.4	141	7.8	96	0.0
June 7, 00	15.7	171	419	7.3	2.4	1.6	11.4	13.5	159	9.1	127	0.0
June 22, 00	16.4	179	226	45.1	2.6	4.5	14.5	17.3	88.5	10.0	141	0.0
July 14, 00	20.8	200	153	30.1	2.5	7.2	23.4	27.8	66.8	15.9	161	0.0
Aug. 8, 00	19.8	457	185	64.7	3.1	22.9	9.8	11.6	113	16.5	187	0.0
Averages	15.1	233	283	25.2	2.9	5.5	26.3	31.2	133	10.9	123	0.0
SD	4.3	110	174	22.4	2.2	8.1	21.2	25.2	46.9	3.7	50	0.0
Donald												
June 10, 99	10.2	157	941	19.3	9.0	5.7	29.7	35.2	198	0.0	5.0	0.0
June 23, 99	12.0	289	578	27.3	0.0	0.0	0.0	0.0	125	3.0	9.7	0.0
July 7, 99	12.3	127	470	12.5	7.7	9.4	27.1	32.2	117	0.0	2.4	0.0
July 20, 99	14.8	148	168	11.8	8.6	2.1	2.2	2.8	105	0.0	0.0	0.0
Aug. 4, 99	15.5	209	109	13.8	20.4	50.2	0.0	0.0	334	0.0	4.5	26
Aug. 19, 99	15.0	140	87.2	8.6	0.0	15.3	33.3	42.1	114	0.0	4.6	0.0
Averages	13.3	178	392	15.6	7.6	13.8	15.4	18.7	165	0.5	4.4	4.3
SD	2.1	61.2	336	6.7	7.5	18.7	16.2	19.8	89.1	1.2	3.2	10.5

Appendix 1 (continued).

Location and Date	Water Temperature at Time of Sampling	α-HCH	γ-HCH	HCB	Heptachlor Epoxide	Dieldrin	α-endosulfan	β-endosulfan	*Sum of 130 PCB Congeners	pp-DDE	pp-DDD	op-DDT
Kananaskis												
May 2, 00	2.6	186	164	13.6	9.6	13.1	14.7	17.5	166	0.0	0.0	0.0
May 18, 00	6.7	160	161	24.8	7.7	9.1	25.5	30.3	101	1.8	2.2	0.0
June 8, 00	9.5	194	167	12.4	4.7	8.0	8.7	10.4	88.5	0.0	0.0	7.5
June 22, 00	11.2	157	143	12.8	0.0	17.9	22.6	26.9	173	8.3	10	0.0
July 14, 00	11.5	107	94.2	11.2	4.6	11.4	6.5	7.7	73.2	0.0	2.5	0.0
Aug. 7, 00	17.0	157	123	13.6	6.2	12.1	9.4	11.2	78.6	4.3	11	11.9
Averages	9.8	160	142	14.7	5.5	11.9	14.6	17.3	113	2.4	4.3	3.2
SD	4.9	30.7	28.6	5.0	3.3	3.5	7.9	9.4	44.5	3.3	4.9	5.2
Dixon Dam												
April 22, 00	2.6	76.8	283	10.1	13.2	3.3	57.8	68.6	62.2	0.0	0.0	0.0
May 10, 00	6.7	80.9	706	24.5	7.4	3.6	21.7	25.8	214	1.0	0.0	0.0
June 3, 00	9.4	61.4	499	9.7	4.3	2.4	6.6	7.8	61.0	2.2	0.0	0.0
June 20, 00	11.5	57.2	650	6.8	4.5	4.2	13.8	16.4	35.1	2.3	4.5	0.0
July 12, 00	12.5	93.5	591	10.8	0.0	10.5	12.3	14.6	123	9.7	6.8	0.0
Aug. 1, 00	17.0	76.4	479	8.4	5.4	9.0	6.1	7.3	66.4	4.5	5.4	0.0
Averages	10.0	74.4	535	11.7	5.8	5.5	19.7	23.4	93.6	3.3	2.8	0.0
SD	5.0	13.3	151	6.4	4.4	3.4	19.5	23.1	65.6	3.5	3.1	0.0

* Sum of 130 PCBs consisted of the following congeners, with dashed lines representing coeluting PCBs: 1,3,4-10, 7-9,6,8-5,19,12-13,18,15-17,24-27,16-32,54-29,26,25,50,31-28,33-20-53,51,22,45,46,52,49,43,48-47,44,59-42,64-41-71,40,100,63,74,70-76-98,66-95,91-55,56-60,92,84,101,99,119,83,97,87-81,85,136,110,82,151,135-144,147-107,149,118,133,114,134-131,146,153-132-105,141-179,137,176-130,163-138,158,129,178,175,187-182,183,128,167,185,174,177,202-171,156,173,157-200,172,197,180,193,191,199,170-190,198,201,203-196,189,206-195,207,194,205,208,209.

Appendix 2. Air concentrations of selected POPs. Averaged air temperatures were calculated during the sample period and all air concentrations are in pg m^{-3}.

Location and Date	Averaged Air Temperatures During Sample Period	α-HCH	γ-HCH	HCB	Heptachlor Epoxide	Dieldrin	α-endosulfan	β-endosulfan	*Sum of 130 PCB Congeners
Bow Lake									
May 18-20, 98	5.1	32.7	45.3	15.2	0.0	0.3	6.9	0.0	28.6
June 6-11, 98	6.7	35.8	45.5	5.7	0.2	0.9	0.3	0.1	11.6
June 22-25, 98	11.3	40.4	15.4	8.6	1.3	0.3	15.5	0.2	12.2
July 4-8, 98	10.9	46.1	21.5	5.6	0.9	0.8	23.0	0.3	13.0
July 27-30, 98	11.9	45.4	2.9	6.5	2.3	0.9	11.8	0.0	19.1
Aug. 8-13, 98	15.0	22.4	7.2	3.4	1.0	0.1	16.7	0.0	8.6
Aug. 25-27, 98	15.0	36.9	6.9	12.5	0.5	0.30	22.1	0.8	7.8
Averages	11.4	35.6	20.5	8.7	0.88	0.47	13.8	0.35	14.6
SD	3.8	8.1	18.0	4.2	0.77	0.34	8.2	0.29	7.3
Bow Lake									
June 4-8, 99	3.7	37.2	12.5	6.5	1.7	0.48	46.7	1.3	11.8
June 16-20, 99	10	47.4	11.4	21.4	1.2	1.4	46.8	0.15	16.9
June 30-Jul. 4, 99	4.4	6.4	0.0	32.7	0.0	1.4	15.5	1.3	65.7
July 28-Aug.1, 99	7.1	45.7	6.2	8.1	0.24	0.22	16.5	0.01	13.9
Aug. 11-13, 99	8.6	42.5	10.5	16	0.38	0.38	14.4	0.05	18.0
Averages	6.8	35.8	8.1	17	0.71	0.77	28.0	0.56	25.3
SD	2.7	16.9	5.12	10.7	0.73	0.57	17.2	0.68	22.7
Bow Lake									
May 9-11, 00	-1.1	3.2	0.4	53.5	0.2	0.9	36.4	1.2	276
June 1-3, 00	1.5	14	3.2	52.8	2.0	3.3	24.2	2.0	80
June 28-30, 00	9.4	63.6	4.3	44.1	2.2	2.5	26.1	4.5	49
July 25-27, 00	9.5	16.9	2.3	23.9	0.0	0.3	12.8	0.1	235
Aug. 15-17, 00	5.6	6.7	1.0	36.2	0.0	2.3	31.8	6.3	89.4
Averages	5.0	20.9	2.3	42.1	0.88	1.9	26.3	2.8	146
SD	4.7	24.5	1.6	12.4	1.1	1.2	8.9	2.5	102

Appendix 2 (continued).

Location and Date	Averaged Air Temperatures During Sample Period	α-HCH	γ-HCH	HCB	Heptachlor Epoxide	Dieldrin	α-endosulfan	β-endosulfan	*Sum of 130 PCB Congeners
Donald									
June 10-14, 99	6.3	22.8	0.51	20.1	0.25	0.03	1.3	0.0	76.5
June 23-27, 99	13.0	8.7	1.8	21.6	0.5	2.9	51.2	7.0	206
July 7-11, 99	12.1	36.2	5.8	19.5	0.24	0.08	4.0	0.12	77
July 20-24, 99	15.0	30.0	17.1	6.2	0.74	0.6	19.3	0.044	70.3
Aug. 4-8, 99	16.5	33.8	16.2	6.3	2.0	0.61	25.5	0.39	108
Averages	12.6	26.3	8.3	14.7	0.74	0.84	20.2	1.5	108
SD	3.9	11.1	7.9	7.8	0.72	1.2	20.1	3.1	57.1
Kananaskis									
May 5-7, 00	5.6	97.6	0.9	200	10.6	12.5	467	3.8	579
May 17-19, 00	7.5	16.0	0.0	27.0	11.1	10.6	477	51.6	619
June 22-24, 00	8.2	4.4	0.3	24.4	0.1	1.1	16.9	1.6	76.8
July 12-14, 00	19.9	42.5	0.0	58.8	3.9	6.1	183	13.5	492
Aug. 7-9, 00	13.2	4.9	0.5	18.5	0.0	0.9	16.8	2.3	323
Averages	10.9	33.1	0.3	65.7	5.3	6.2	232	14.6	418
SD	5.8	39.2	0.38	76.6	5.4	5.3	229	21.3	222
Dixon Dam									
May 29-31, 00	11.7	3.7	0.0	36.7	0.0	0.2	4.5	0.0	177
July 10-12, 00	15.8	29.4	119	14.6	3.1	2.9	34.8	4.2	94.8
July 31-Aug.1, 00	18.4	9.9	1.2	39.3	2.4	6.6	53.2	10.3	245
Averages	15.3	14.3	40.2	30.2	1.8	3.2	30.8	4.8	172
SD	3.4	13.4	68.6	13.6	1.6	3.2	24.6	5.2	75.3

* Sum of 130 PCBs consisted of the following congeners, with dashes representing coeluting PCBs: 1,3,4-10, 7-9,6,8-5,19,12-13,18,15-17,24-27,16-32,54-29,26,25,50,31-28,33-20-53,51,22,45,46,52,49,43,48-47,44,59-42,64-41-71,40,100,63,74,70-76-98,66-95,91-55,56-60,92,84,101,99,119,83,97,87-81,85,136,110,82,151,135-144,147-107,149,118,133,114,134-131,146,153-132-105,141-179,137,176-130,163-138,158,129,178,175,187-182,183,128,167,185,174,177,202-171,156,173,157-200,172,197,180,193,191,199,170-190,198,201,203-196,189,206-195,207,194,205,208,209.

Appendix 3. Air and water-phase concentrations of six different organochlorines, collected concurrently. Fluxes were calculated using the two-film resistance model (see text).

γ-HCH	Lake	$C_{a,g}$	$C_{w,d}$	T_a	T_i	Flux
Sample Date		(pg m^{-3})[a]	(pg L^{-1})[b]	(kelvin)[c]	(kelvin)[d]	(ng m^{-2} d^{-1})
May 18, 98	Bow	45	35	278.1	279.5	-38
June 6, 98		46	60	279.7	280.7	-37
June 22, 98		15	44	284.3	282.6	-7.1
July 4, 98		22	95	283.9	285.7	-7.3
July 27, 98		2.9	94	284.9	288.4	2.1
Aug. 8, 98		7.2	46	288.0	287.3	-1.6
Aug. 25, 98		6.9	64	288.0	283.0	-2.1
June 4, 99		13	730	276.7	274.8	20
June 16, 99		11	380	283.0	280.9	16
June 30, 99		0.0	480	277.4	282.5	44
July 28, 99		6.2	240	280.1	282.0	6.5
Aug. 11, 99		11	160	281.6	286.9	2.6
May 9, 00		0.4	160	271.9	273.4	1.4
June 1, 00		3.2	160	274.5	276.1	0.6
June 28, 00		4.3	110	282.4	282.0	1.5
July 25, 00		2.3	130	282.5	283.5	5.4
Aug 15, 00		1.0	100	278.6	282.2	6.0
June 10, 99	Donald	0.51	940	279.3	283.2	73
June 23, 99		1.8	580	286.0	285.0	60
July 7, 99		5.8	470	285.1	285.3	25
July 20, 99		17	170	288.0	287.8	-5.5
Aug. 4, 99		16	110	289.5	288.5	-10
May 5, 00	Kananaskis	0.9	160	278.6	275.6	2.0
May 19, 00		0.0	160	280.5	279.7	5.5
June 22, 00		0.3	140	281.2	284.2	6.4
July 12, 00		0.0	94	292.9	284.5	2.0
Aug. 7, 00		0.5	120	286.2	290.0	7.2
May 29, 00	Dixon Dam	0 .0	500	284.7	282.4	14
July 10, 00		120	590	288.8	285.5	-41
July 31, 00		1.2	480	291.4	290.0	16

[a] $C_{a,g}$, gas-phase concentrations of γ-HCH. [b] $C_{w,d}$, dissolved water concentrations of γ-HCH. [c] T_a, air temperature in Kelvin. [d] T_i, air-water interface temperature in Kelvin.

Appendix 3 (continued).

α-HCH	Lake	C_a	C_w	T_a	T_i	Flux
Sample Date		(pg m^{-3})	(pg L^{-1})	(kelvin)	(kelvin)	(ng m^{-2} d^{-1})
May 18, 98	Bow	33	150	278.1	279.5	-14
June 6, 98		36	57	279.7	280.7	-22
June 22, 98		40	110	284.3	282.6	-20
July 4, 98		46	110	283.9	285.7	-12
July 27, 98		45	140	284.9	288.4	-7.8
Aug. 8, 98		22	70	288.0	287.3	-4.6
Aug. 25, 98		37	110	288.0	283.0	-14
June 4, 99		37	580	276.7	274.8	-9.6
June 16, 99		47	630	283.0	280.9	11
June 30, 99		6.4	340	277.4	282.5	33
July 28, 99		46	460	280.1	282.0	-1.8
Aug. 11, 99		43	310	281.6	286.9	1.1
May 9, 00		3.2	280	271.9	273.4	3.5
June 1, 00		14	180	274.5	276.1	-0.8
June 28, 00		64	190	282.4	282.0	-43
July 25, 00		17	250	282.5	283.5	7.9
Aug 15, 00		6.7	200	278.6	282.2	12
June 10, 99	Donald	23	160	279.3	283.2	-6.6
June 23, 99		8.7	290	286.0	285.0	29
July 7, 99		36	130	285.1	285.3	-16
July 20, 99		30	150	288.0	287.8	-7.0
Aug. 4, 99		34	210	289.5	288.5	-1.3
May 5, 00	Kananaskis	98	190	278.6	275.6	-37
May 19, 00		16	160	280.5	279.7	-2.3
June 22, 00		4.4	160	281.2	284.2	8.7
July 12, 00		44	110	292.9	284.5	-9.4
Aug. 7, 00		4.9	160	286.2	290.0	12
May 29, 00	Dixon Dam	3.7	61	284.7	282.4	1.1
July 10, 00		29	94	288.8	285.5	-8.3
July 31, 00		9.9	76	291.4	290.0	1.2

[a] $C_{a,g}$, gas-phase concentrations of α-HCH. [b] $C_{w,d}$, dissolved water concentrations of α-HCH. [c] T_a, air temperature in Kelvin. [d] T_i, air-water interface temperature in Kelvin.

Appendix 3 (continued).

HCB	Lake	C_a	C_w	T_a	T_i	Flux
Sample Date		(pg m^{-3})	(pg L^{-1})	(kelvin)	(kelvin)	(ng m^{-2} d^{-1})
May 18, 98	Bow	15	5.3	278.1	279.5	6.9
June 6, 98		5.7	2.8	279.7	280.7	7.2
June 22, 98		8.6	3.1	284.3	282.6	3.7
July 4, 98		5.6	3.1	283.9	285.7	3.5
July 27, 98		6.5	4.8	284.9	288.4	5.3
Aug. 8, 98		3.4	4.9	288.0	287.3	5.6
Aug. 25, 98		13	3.4	288.0	283.0	2.5
June 4, 99		6.5	23	276.7	274.8	4.0
June 16, 99		21	21	283.0	280.9	3.2
June 30, 99		33	16	277.4	282.5	2.3
July 28, 99		8.1	16	280.1	282.0	2.6
Aug. 11, 99		16	23	281.6	286.9	3.9
May 9, 00		54	16	271.9	273.4	1.8
June 1, 00		53	56	274.5	276.1	27
June 28, 00		44	16	282.4	282.0	2.0
July 25, 00		24	11	282.5	283.5	1.6
Aug 15, 00		36	19	278.6	282.2	2.7
June 10, 99	Donald	20	19	279.3	283.2	3.2
June 23, 99		22	27	286.0	285.0	4.5
July 7, 99		20	13	285.1	285.3	2.1
July 20, 99		6.2	12	288.0	287.8	2.0
Aug. 4, 99		6.3	14	289.5	288.5	2.1
May 5, 00	Kananaskis	200	14	278.6	275.6	-9.9
May 19, 00		27	25	280.5	279.7	5.0
June 22, 00		24	13	281.2	284.2	2.4
July 12, 00		59	11	292.9	284.5	0.8
Aug. 7, 00		19	14	286.2	290.0	2.2
May 29, 00	Dixon Dam	37	9.7	284.7	282.4	1.6
July 10, 00		15	11	288.8	285.5	3.0
July 31, 00		39	8.4	291.4	290.0	2.3

[a] $C_{a,g}$, gas-phase concentrations of HCB. [b] $C_{w,d}$, dissolved water concentrations of HCB. [c] T_a, air temperature in Kelvin. [d] T_i, air-water interface temperature in Kelvin.

Appendix 3 (continued).

Dieldrin	Lake	C_a	C_w	T_a	T_i	Flux
Sample Date		(pg m^{-3})	(pg L^{-1})	(kelvin)	(kelvin)	(ng m^{-2} d^{-1})
May 18, 98	Bow	0.37	8.3	278.1	279.5	1.1
June 6, 98		0.97	4.3	279.7	280.7	0.36
June 22, 98		0.37	6.8	284.3	282.6	0.96
July 4, 98		0.85	8.5	283.9	285.7	1.3
July 27, 98		0.9	8.5	284.9	288.4	1.4
Aug. 8, 98		0.1	5.2	288.0	287.3	0.89
Aug. 25, 98		0.3	6.7	288.0	283.0	0.81
June 4, 99		0.48	37	276.7	274.8	4.9
June 16, 99		1.4	0.0	283.0	280.9	-0.44
June 30, 99		1.4	24	277.4	282.5	3.4
July 28, 99		0.22	20	280.1	282.0	2.7
Aug. 11, 99		0.38	13	281.6	286.9	2.0
May 9, 00		0.9	22	271.9	273.4	1.3
June 1, 00		3.3	28	274.5	276.1	1.1
June 28, 00		2.5	20	282.4	282.0	2.4
July 25, 00		0.3	22	282.5	283.5	3.1
Aug 15, 00		2.3	25	278.6	282.2	3.0
June 10, 99	Donald	0.03	5.7	279.3	283.2	0.88
June 23, 99		2.9	0.0	286.0	285.0	-0.63
July 7, 99		0.08	9.4	285.1	285.3	1.5
July 20, 99		0.6	2.1	288.0	287.8	0.23
Aug. 4, 99		0.61	50	289.5	288.5	7.5
May 5, 00	Kananaskis	13	13	278.6	275.6	-2.7
May 19, 00		11	9.1	280.5	279.7	-2.1
June 22, 00		1.1	18	281.2	284.2	2.7
July 12, 00		6.1	11	292.9	284.5	0.28
Aug. 7, 00		0.9	12	286.2	290.0	1.7
May 29, 00	Dixon Dam	0.2	2.4	284.7	282.4	0.31
July 10, 00		2.9	11	288.8	285.5	1.2
July 31, 00		6.6	9.0	291.4	290.0	0.71

[a] $C_{a,g}$, gas-phase concentrations of dieldrin. [b] $C_{w,d}$, dissolved water concentrations of dieldrin. [c] T_a, air temperature in Kelvin. [d] T_i, air-water interface temperature in Kelvin.

Appendix 3 (continued).

α-endosulfan	Lake	Ca	Cw	Ta	Ti	Flux
Sample Date		(pg m^{-3})	(pg L^{-1})	(kelvin)	(kelvin)	(ng m^{-2} d^{-1})
May 18, 98	Bow	6.9	6.0	278.1	279.5	-3.4
June 6, 98		0.3	4.0	279.7	280.7	0.26
June 22, 98		16	0.0	284.3	282.6	-9.6
July 4, 98		23	4.1	283.9	285.7	-12
July 27, 98		12	7.7	284.9	288.4	-5.8
Aug. 8, 98		17	5.7	288.0	287.3	-9.8
Aug. 25, 98		22	3.5	288.0	283.0	-10
June 4, 99		47	20	276.7	274.8	-28
June 16, 99		47	0.0	283.0	280.9	-38
June 30, 99		16	20	277.4	282.5	-9.1
July 28, 99		17	12	280.1	282.0	-7.8
Aug. 11, 99		14	21	281.6	286.9	-8.6
May 9, 00		36	10	271.9	273.4	-9.0
June 1, 00		24	12	274.5	276.1	-4.5
June 28, 00		26	12	282.4	282.0	-14
July 25, 00		13	45	282.5	283.5	-2.6
Aug 15, 00		32	28	278.6	282.2	-17
June 10, 99	Donald	1.3	30	279.3	283.2	2.7
June 23, 99		51	0.0	286.0	285.0	-39
July 7, 99		4.0	27	285.1	285.3	0.49
July 20, 99		19	2.2	288.0	287.8	-13
Aug. 4, 99		25	0.0	289.5	288.5	-19
May 5, 00	Kananaskis	470	15	278.6	275.6	-160
May 19, 00		480	26	280.5	279.7	-230
June 22, 00		17	23	281.2	284.2	-6.5
July 12, 00		180	6.5	292.9	284.5	-46
Aug. 7, 00		17	9.4	286.2	290.0	-7.3
May 29, 00	Dixon Dam	4.5	6.6	284.7	282.4	-1.3
July 10, 00		35	12	288.8	285.5	-13
July 31, 00		53	6.1	291.4	290.0	-17

[a] $C_{a,g}$, gas-phase concentrations of α-endosulfan. [b] $C_{w,d}$, dissolved water concentrations of α-endosulfan . [c] T_a, air temperature in Kelvin. [d] T_i, air-water interface temperature in Kelvin.

Appendix 3 (continued).

β-endosulfan	Lake	Ca	Cw	Ta	Ti	Flux
Sample Date		(pg m^{-3})	(pg L^{-1})	(kelvin)	(kelvin)	(ng m^{-2} d^{-1})
May 18, 98	Bow	0.0	4.0	278.1	279.5	0.5
June 6, 98		0.1	3.0	279.7	280.7	0.33
June 22, 98		0.2	4.0	284.3	282.6	0.41
July 4, 98		0.3	0.0	283.9	285.7	-0.14
July 27, 98		0.0	0.0	284.9	288.4	0.0
Aug. 8, 98		0.0	3.8	288.0	287.3	0.41
Aug. 25, 98		0.8	3.5	288.0	283.0	0.03
June 4, 99		1.3	23	276.7	274.8	2.6
June 16, 99		0.2	0.0	283.0	280.9	-0.09
June 30, 99		1.3	24	277.4	282.5	2.7
July 28, 99		0.01	14	280.1	282.0	1.6
Aug. 11, 99		0.1	26	281.6	286.9	3.9
May 9, 00		1.2	12	271.9	273.4	0.54
June 1, 00		2.0	7.5	274.5	276.1	0.01
June 28, 00		4.5	14	282.4	282.0	-0.4
July 25, 00		0.1	53	282.5	283.5	5.9
Aug 15, 00		6.3	34	278.6	282.2	1.1
June 10, 99	Donald	0.0	35	279.3	283.2	4.6
June 23, 99		7.0	0.0	286.0	285.0	-4.1
July 7, 99		0.12	32	285.1	285.3	3.8
July 20, 99		0.044	2.8	288.0	287.8	0.34
Aug. 4, 99		0.39	0.0	289.5	288.5	-0.22
May 5, 00	Kananaskis	3.8	18	278.6	275.6	0.31
May 19, 00		52	30	280.5	279.7	-18
June 22, 00		1.6	27	281.2	284.2	2.2
July 12, 00		14	7.7	292.9	284.5	-2.6
Aug. 7, 00		2.3	11	286.2	290.0	0.12
May 29, 00	Dixon Dam	0.0	7.8	284.7	282.4	0.7
July 10, 00		4.2	15	288.8	285.5	-0.23
July 31, 00		10	7.3	291.4	290.0	-2.7

[a] $C_{a,g}$, gas-phase concentrations of β-endosulfan. [b] $C_{w,d}$, dissolved water concentrations of β-endosulfan. [c] T_a, air temperature in Kelvin. [d] T_i, air-water interface temperature in Kelvin.

Appendix 4. Water chemistry of selected lakes at the time of sampling. Water temperature, air temperature and wind speed, were also taken at the time of sampling. PON is particulate organic nitrogen, TP is total phosphorus, DOC is dissolved organic carbon, POC is particulate organic carbon, Alk is alkalinity as $CaCO_3$, Cond is conductivity, and TN is total nitrogen.

	Bow Outflow, 1999										
Site	**Site Data**	**NH_4^+ (µg/L)**	**$NO_2^-NO_3$ (µg/L)**	**PON (µg/L)**	**TP (µg/L)**	**DOC (mg/L)**	**POC (µg/L)**	**Ca (mg/L)**	**Mg (mg/L)**	**Alk (mg/L)**	**HCO_3^- (mg/L)**
Bow Outflow	June 4, 99	N/A	N/A	3.5	3.0	1.6	77.1	N/A	N/A	N/A	N/A
	June 16, 99	N/A	N/A	27.0	3.4	1.3	620	18.5	8.5	66.5	81.1
	June 30, 99	3.9	27.1	31.6	3.9	0.85	502	18.5	9.0	68.9	84.0
	July 17, 99	N/A	N/A	22.3	3.9	0.73	422	19.2	8.9	69.5	84.8
	July 31, 00	N/A	N/A	27.0	8.2	0.53	427	19.5	9.0	69.6	84.8
	Aug. 11, 99	N/A	N/A	28.2	2.6	0.83	364	19.8	8.7	69.3	84.5

Site Data	**CO_3^{2-} (mg/L)**	**Cond (µS/cm)**	**pH**	**TN (µg/L)**	**Chl-*a* (µg/L)**	**Water Temperature at Time of Sampling**	**24-hour Averaged Air Temperature**	**Averaged Wind Speed During Sample Period (m/s)**
June 4, 99	N/A	163	N/A	201	N/A	1.8	3.8	0.63
June 16, 99	N/A	162	7.9	134	N/A	7.9	9.5	0.30
June 30, 99	N/A	172	7.8	119	0.18	9.5	5.7	0.53
July 17, 99	N/A	167	7.9	103	N/A	9.0	2.5	N/A
July 31, 00	N/A	173	7.8	131	0.18	9.0	13.4	1.1
Aug. 11, 99	N/A	168	7.8	121	0.09	13.9	10.5	0.28

Appendix 4 (continued).

	Bow Outflow, 2000									
Site	**Site Data**	**PON (µg/L)**	**TP (µg/L)**	**DOC (mg/L)**	**POC (µg/L)**	**Ca (mg/L)**	**Mg (mg/L)**	**Alk (mg/L)**	**HCO_3^- (mg/L)**	**CO_3^{2-} (mg/L)**
Bow Outflow	April 25, 00	23.8	2.3	10.3	398	21.6	10.4	80.2	97.8	N/A
	May 9, 00	18.0	2.1	0.46	196	21.5	9.6	75.4	91.9	N/A
	May 30, 00	20.0	2.3	1.5	489	46.7	9.1	72.7	88.6	N/A
	June 13, 00	14.4	2.8	0.67	244	19.3	9.0	70.3	85.7	N/A
	June 28, 00	11.7	1.5	0.52	228	21.2	9.3	73.9	90.1	N/A
	July 27, 00	14.6	1.8	0.53	355	19.7	9.2	73.1	89.2	N/A
	Aug. 15, 00	103	1.2	0.58	708	19.3	9.0	68.3	83.3	N/A

Site Data	**Cond (µS/cm)**	**pH**	**TN (µg/L)**	**Chl-*a* (µg/L)**	**Water Temperature at Time of Sampling**	**24-hour Averaged Air Temperature**	**Averaged Wind Speed During Sample Period (m/s)**
April 25, 00	198	7.3	130	0.07	0.4	-5.2	6.1
May 9, 00	185	8.2	62.0	0.08	1.4	-1.1	5.0
May 30, 00	172	8.0	121	0.12	3.1	1.5	7.0
June 13, 00	170	8.1	101	0.13	3.5	4.9	1.0
June 28, 00	177	8.1	103	0.11	9.0	9.4	0.9
July 27, 00	175	8.2	110	0.15	10.5	9.5	1.0
Aug. 15, 00	169	8.1	104	0.10	9.2	5.6	0.7

Appendix 4 (continued).

	Bow Glacial Stream, 1999										
Site	**Site Data**	**NH_4^+ (µg/L)**	**$NO_2^+NO_3$ (µg/L)**	**PN (µg/L)**	**TOP (µg/L)**	**DOC (mg/L)**	**POC (µg/L)**	**Ca (mg/L)**	**Mg (mg/L)**	**Alk (mg/L)**	**HCO_3^- (mg/L)**
Bow Glacial	June 5, 99	N/A	N/A	33.6	3.0	0.50	944	N/A	N/A	N/A	N/A
	June 18, 99	N/A	N/A	30.5	9.8	0.56	886	23.6	10.6	87.1	106
	July 1, 99	4.35	108	29.3	3.5	0.26	429	19.6	8.5	66.2	80.7
	July 15, 99	N/A	N/A	22.3	3.7	0.47	592	23.6	10.6	73.0	89.0
	July 29, 99	N/A	N/A	37.6	16.5	0.36	893	20.2	8.2	67.3	82.0
	Aug. 12, 99	N/A	N/A	25.8	3.4	0.18	781	15.4	5.2	46.2	56.4

Site Data	**CO_3^{2-} (mg/L)**	**Cond (µS/cm)**	**pH**	**TN (µg/L)**	**Chl-*a* (µg/L)**	**Water Temperature at Time of Sampling**	**24-hour Averaged Air Temperature**	**Averaged Wind Speed During Sample Period (m/s)**
June 5, 99	N/A	196	N/A	341	N/A	2.5	7.9	0.63
June 18, 99	N/A	208	7.89	148	N/A	3.8	10.1	0.30
July 1, 99	N/A	170	7.84	190	0.03	4.7	6.6	0.53
July 15, 99	N/A	177	7.81	139	N/A	2.5	4.9	N/A
July 29, 99	N/A	169	7.69	134	0.03	5.7	14	1.1
Aug. 12, 99	N/A	119	7.62	259	0.05	6.5	10.6	0.28

Appendix 4 (continued).

	Bow Glacial Stream, 2000									
Site	**Site Data**	**PON (µg/L)**	**TP (µg/L)**	**DOC (mg/L)**	**POC (µg/L)**	**Ca (mg/L)**	**Mg (mg/L)**	**Alk (mg/L)**	**HCO_3^- (mg/L)**	**CO_3^{2-} (mg/L)**
Bow Glacial	April, 24, 00	22.8	2.0	0.0	402	22.3	10.7	78.6	95.8	N/A
	May 11, 00	29.4	2.1	0.1	574	25.2	12.3	88.5	108	N/A
	June 1, 00	42.0	2.9	0.2	313	29.3	14.0	81.7	99.6	N/A
	June 15, 00	17.0	5.7	0.3	641	21.4	8.6	71.4	87.1	N/A
	June 28, 00	39.0	2.6	0.3	468	16.0	5.5	48.7	59.3	N/A
	July 25, 00	14.4	2.8	0.4	198	29.3	13.7	85.1	103	0.5
	Aug. 17, 00	15.3	8.4	0.5	528	25.6	11.4	83.8	102	N/A

Site Data	**Cond (µS/cm)**	**pH**	**TN (µg/L)**	**Chl-*a* (µg/L)**	**Water temperature at time of sampling**	**24-hour averaged air temperature**	**Averaged wind speed during sample period (m/s)**
April, 24, 00	199	7.6	119	0.1	0.8	-5.2	6.1
May 11, 00	225	8.3	87.6	0.0	3.5	-1.1	5.0
June 1, 00	261	8.2	114	0.0	0.8	1.5	7.0
June 15, 00	175	8.1	170	0.0	5.0	4.9	1.0
June 28, 00	132	8.1	147	0.1	7.8	9.4	0.9
July 25, 00	254	8.1	215	0.0	4.4	9.5	1.0
Aug. 17, 00	205	7.9	319	0.1	9.0	5.6	0.7

Appendix 4 (continued).

	Rock Isle, 1999										
Site	**Site Data**	**NH_4^+ (µg/L)**	**$NO_2^+NO_3$ (µg/L)**	**PON (µg/L)**	**TP (µg/L)**	**DOC (mg/L)**	**POC (µg/L)**	**Ca (mg/L)**	**Mg (mg/L)**	**Alk (mg/L)**	**HCO_3^- (mg/L)**
Rock Isle	July 2, 99	11.8	22.4	N/A	5.1	0.68	N/A	12.2	3.8	42.7	52.0
	July 8, 99	9.7	16.8	N/A	5.1	0.96	N/A	16.5	5.4	60.3	73.5
	July 23, 99	N/A	N/A	N/A	5.4	1.0	N/A	20.5	6.8	75.4	91.9
	Aug. 6, 99	N/A	N/A	N/A	12.0	0.98	N/A	20.8	7.1	76.1	92.7
	Aug. 18, 99	N/A	N/A	N/A	5.8	1.2	N/A	N/A	N/A	75.3	91.8

Site Data	**CO_3^{2-} (mg/L)**	**Cond (µS/cm)**	**pH**	**TN (µg/L)**	**Chl-*a* (µg/L)**	**Water Temperature at Time of Sampling**	**24-hour Averaged Air Temperature**	**Averaged Wind Speed During Sample Period (m/s)**
July 2, 99	N/A	88.3	7.4	N/A	N/A	0.9	4.2	N/A
July 8, 99	N/A	123	7.7	N/A	N/A	1.7	6.0	N/A
July 23, 99	N/A	152	7.9	N/A	N/A	10.0	8.1	N/A
Aug. 6, 99	N/A	156	8.0	N/A	N/A	12.8	12.0	N/A
Aug. 18, 99	N/A	155	8.0	N/A	N/A	12.0	10.5	N/A

Appendix 4 (continued).

	Rock Isle, 2000									
Site	**Site Data**	**PON (µg/L)**	**TP (µg/L)**	**DOC (mg/L)**	**POC (µg/L)**	**Ca (mg/L)**	**Mg (mg/L)**	**Alk (mg/L)**	**HCO_3^- (mg/L)**	**CO_3^{2-} (mg/L)**
Rock Isle	June 17, 00	63.5	10.2	0.092	666	1.7	0.54	8.0	9.8	N/A
	June 29, 00	35.2	4.3	0.63	370	25.3	3.3	44.5	54.2	N/A
	July 27, 00	17.0	3.9	1.1	308	22.4	7.3	76.3	93.1	N/A
	Aug. 16, 00	14.6	1.8	1.0	286	21.8	7.5	79.8	91.7	2.8
Site Data	**Cond (µS/cm)**	**pH**	**TN (µg/L)**	**Chl-*a* (µg/L)**	**Water Temperature at Time of Sampling**		**24-hour Averaged Air Temperature**		**Averaged Wind Speed During Sample Period (m/s)**	
June 17, 00	17.4	6.7	244	1.5	0.2		4.0		N/A	
June 29, 00	90.1	7.5	68.0	0.49	2.3		9.2		N/A	
July 27, 00	154	8.3	156	0.38	12.8		9.9		N/A	
Aug. 16, 00	161	8.4	203	0.37	13.0		5.8		N/A	

Appendix 4 (continued).

	Wapta, 1999										
Site	**Site Data**	**NH_4^+ (µg/L)**	**$NO_2^+NO_3$ (µg/L)**	**PON (µg/L)**	**TP (µg/L)**	**DOC (mg/L)**	**POC (µg/L)**	**Ca (mg/L)**	**Mg (mg/L)**	**Alk (mg/L)**	**HCO_3^- (mg/L)**
Wapta	June 4, 99	N/A	N/A	22.4	2.4	1.2	281	N/A	N/A	N/A	N/A
	June 16, 99	N/A	N/A	71.6	8.7	0.94	1,400	20.4	8.1	71.1	86.6
	June 30, 99	5.5	110.80	34.0	4.1	0.61	587	20.3	8.8	72.2	88.0
	July 14, 99	N/A	N/A	36.3	14.3	0.55	876	18.7	7.8	66.1	80.6
	July 30, 99	N/A	N/A	21.1	7.2	0.42	334	19.3	8.4	67.2	82.0
	Aug. 11, 99	N/A	N/A	54.0	8.8	0.37	898	18.8	7.9	63.6	77.5

Site Data	**CO_3^{2-} (mg/L)**	**Cond (µS/cm)**	**pH**	**TN (µg/L)**	**Chl-*a* (µg/L)**	**Water Temperature at Time of Sampling**	**24-hour Averaged Air Temperature**	**Averaged Wind Speed During Sample Period (m/s)**
June 4, 99	N/A	211	N/A	290	N/A	6.3	6.5	N/A
June 16, 99	N/A	178	7.8	248	N/A	7.2	14.9	N/A
June 30, 99	N/A	180	7.9	173	0.10	7.5	8.3	N/A
July 14, 99	N/A	161	7.7	213	N/A	7.0	8.0	N/A
July 30, 99	N/A	168	7.8	187	0.07	8.3	10.2	N/A
Aug. 11, 99	N/A	155	7.8	131	0.54	10.5	13.4	N/A

Appendix 4 (continued).

	Wapta, 2000									
Site	**Site Data**	**PON (µg/L)**	**TP (µg/L)**	**DOC (mg/L)**	**POC (µg/L)**	**Ca (mg/L)**	**Mg (mg/L)**	**Alk (mg/L)**	**HCO_3^- (mg/L)**	**CO_3^{2-} (mg/L)**
Wapta	April 19, 00	20.5	2.9	5.5	238	28.4	12.4	102	124	N/A
	May 3, 00	33.6	3.9	0.48	667	25.2	10.6	88.0	101	3.4
	May 16, 00	21.6	3.2	0.47	253	29.1	11.9	100	116	3.3
	June 7, 00	27.6	4.2	0.70	370	24.4	9.7	84.0	102	N/A
	June 22, 00	7.3	1.9	0.87	255	22.0	9.2	76.0	92.6	N/A
	July 13, 00	0.000001	3.2	0.57	264	19.2	8.1	66.6	81.2	N/A
	Aug. 8, 00	1.2	3.9	0.39	213	18.4	7.6	64.3	78.3	N/A

Site Data	**Cond (µS/cm)**	**pH**	**TN (µg/L)**	**Chl-*a* (µg/L)**	**Water Temperature at Time of Sampling**	**24-hour Averaged Air Temperature**	**Averaged Wind Speed During Sample Period (m/s)**
April 19, 00	251	7.6	137	0.069	0.7	6.7	N/A
May 3, 00	215	8.3	167	0.64	2.1	2.6	N/A
May 16, 00	243	8.3	106	0.13	5.2	5.1	N/A
June 7, 00	208	8.1	211	0.38	7.5	8.1	N/A
June 22, 00	181	8.0	121	0.20	7.0	7.1	N/A
July 13, 00	162	8.1	157	0.10	7.2	12.9	N/A
Aug. 8, 00	155	8.2	257	0.12	8.5	10.9	N/A

Appendix 4 (continued).

	Vermilion, 1999										
Site	**Site Data**	**NH_4^+ (µg/L)**	**$NO_2^+NO_3$ (µg/L)**	**PON (µg/L)**	**TP (µg/L)**	**DOC (mg/L)**	**POC (µg/L)**	**Ca (mg/L)**	**Mg (mg/L)**	**Alk (mg/L)**	**HCO_3^- (mg/L)**
Vermilion	June 11, 99	N/A	N/A	63.9	12.0	3.4	734	N/A	N/A	N/A	N/A
	June 23, 99	N/A	N/A	107	22.0	3.4	980	45.5	15.1	124	151
	July 7, 99	16.7	43.4	70.3	14.9	4.1	906	48.5	16.6	129	158
	July 20, 99	N/A	N/A	78.5	17.9	5.6	758	54.4	9.7	140	171
	Aug. 3, 99	N/A	N/A	69.2	19.4	0.72	812	21.5	8.6	132	140
	Aug. 19, 99	N/A	N/A	50.4	13.0	4.4	568	49.8	20.7	133	146

Site Data	**CO_3^{2-} (mg/L)**	**Cond (µS/cm)**	**pH**	**TN (µg/L)**	**Chl-*a* (µg/L)**	**Water Temperature at Time of Sampling**	**24-hour Averaged Air Temperature**	**Averaged Wind Speed During Sample Period (m/s)**
June 11, 99	N/A	523	N/A	N/A	N/A	12.0	8.5	1.8
June 23, 99	N/A	349	8.0	331	N/A	12.2	10.6	2.6
July 7, 99	N/A	386	8.2	325	1.7	13.0	10.9	2.2
July 20, 99	N/A	438	8.0	424	N/A	17.0	13.2	1.9
Aug. 3, 99	9.9	445	8.4	430	0.77	23.9	16.9	1.5
Aug. 19, 99	7.9	451	8.4	269	0.97	20.0	15.4	1.9

Appendix 4 (continued).

	Vermilion, 2000									
Site	**Site Data**	**PON (µg/L)**	**TP (µg/L)**	**DOC (mg/L)**	**POC (µg/L)**	**Ca (mg/L)**	**Mg (mg/L)**	**Alk (mg/L)**	**HCO_3^- (mg/L)**	**CO_3^{2-} (mg/L)**
Vermilion	April 18, 00	79.5	14.9	1.9	780	35.5	12.0	93.9	114	N/A
	May 4, 00	60.1	7.4	1.0	526	60.5	20.7	124	148	1.6
	May 17, 00	63.6	8.9	1.2	652	62.4	21.3	126	143	5.2
	June 7, 00	66.0	9.6	1.5	642	64.5	22.6	131	159	N/A
	June 22, 00	26.7	5.3	1.8	445	70.3	24.0	134	164	N/A
	July 14, 00	25.5	8.4	2.0	423	70.1	24.0	137	167	N/A
	Aug. 8, 00	46.3	9.4	2.1	582	14.0	24.8	138	168	N/A

Site Data	**Cond (µS/cm)**	**pH**	**TN (µg/L)**	**Chl-*a* (µg/L)**	**Water Temperature at Time of Sampling**	**24-hour Averaged Air Temperature**	**Averaged Wind Speed During Sample Period (m/s)**
April 18, 00	313	7.4	340	0.84	10.0	4.4	N/A
May 4, 00	566	8.3	129	0.90	10.4	6.1	N/A
May 17, 00	581	8.4	129	0.61	12.8	7.6	N/A
June 7, 00	606	8.2	197	1.1	15.7	12.5	N/A
June 22, 00	629	8.0	170	0.48	16.4	10.3	N/A
July 14, 00	641	8.1	301	0.84	20.8	18.9	N/A
Aug. 8, 00	651	8.3	117	1.5	19.8	13.7	N/A

Appendix 4 (continued).

	Donald, 1999										
Site	**Site Data**	**NH_4^+ (µg/L)**	**$NO_2^+NO_3$ (µg/L)**	**PON (µg/L)**	**TP (µg/L)**	**DOC (mg/L)**	**POC (µg/L)**	**Ca (mg/L)**	**Mg (mg/L)**	**Alk (mg/L)**	**HCO_3^- (mg/L)**
Donald	June 10, 99	N/A	N/A	25.8	20.5	1.4	711	N/A	N/A	N/A	N/A
	June 23, 99	N/A	N/A	N/A	93.1	1.9	N/A	22.9	8.1	80.6	98.3
	July 7, 99	N/A	N/A	N/A	47.7	1.2	N/A	24.2	10.1	88.4	108
	July 20, 99	N/A	N/A	N/A	35.9	1.2	N/A	22.4	8.9	78.1	95.2
	Aug. 4, 99	N/A	N/A	N/A	30.6	5.8	N/A	51.0	22.4	73.0	89.0
	Aug. 19, 99	N/A	N/A	17.2	0.82	N/A	N/A	N/A	71.1	86.7	N/A

Site Data	**CO_3^{2-} (mg/L)**	**Cond (µS/cm)**	**pH**	**TN (µg/L)**	**Chl-*a* (µg/L)**	**Water Temperature at Time of Sampling**	**24-hour Averaged Air Temperature**	**Averaged Wind Speed During Sample Period (m/s)**
June 10, 99	N/A	217	N/A	N/A	N/A	10.2	6.3	0.76
June 23, 99	N/A	187	7.9	N/A	N/A	12.0	13.0	0.41
July 7, 99	N/A	203	8.0	N/A	N/A	12.3	12.1	1.2
July 20, 99	N/A	185	7.8	N/A	N/A	14.8	15.0	0.63
Aug. 4, 99	N/A	177	7.8	N/A	N/A	15.5	16.5	0.49
Aug. 19, 99	178	7.8	N/A	N/A	N/A	15.0	17.1	0.32

Appendix 4 (continued).

	Kananaskis, 2000									
Site	**Site Data**	**PON (µg/L)**	**TP (µg/L)**	**DOC (mg/L)**	**POC (µg/L)**	**Ca (mg/L)**	**Mg (mg/L)**	**Alk (mg/L)**	**HCO_3^- (mg/L)**	**CO_3^{2-} (mg/L)**
Kananaskis	May 2, 00	62.5	6.9	0.60	802	32.8	5.5	92.3	113	N/A
	May 18, 00	49.2	8.4	0.80	534	33.2	5.6	96.8	118	N/A
	June 8, 00	62.4	5.4	0.49	605	35.1	6.3	97.0	118	N/A
	June 22, 00	56.3	6.6	0.95	595	36.9	6.8	103	125	N/A
	July 14, 00	70.5	14.2	0.93	824	38.4	8.2	108	131	N/A
	Aug. 7, 00	53.6	7.8	1.08	530	37.3	7.7	104	120	3.4
Site Data	**Cond (µS/cm)**	**pH**	**TN (µg/L)**	**Chl-*a* (µg/L)**	**Water Temperature at Time of Sampling**		**24-hour Averaged Air Temperature**		**Averaged Wind Speed During Sample Period (m/s)**	
May 2, 00	207	8.3	85.7	0.99	2.6		5.6		3.4	
May 18, 00	219	8.3	62.2	1.2	6.7		7.5		1.8	
June 8, 00	217	8.2	101	1.5	9.5		11.0		N/A	
June 22, 00	225	8.2	138	1.2	11.2		8.2		1.7	
July 14, 00	247	8.3	172	2.0	11.5		20.0		3.9	
Aug. 7, 00	235	8.5	164	0.99	17.0		13.2		1.5	

Appendix 4 (continued).

	Dixon Dam, 2000									
Site	**Site Data**	**PON (µg/L)**	**TP (µg/L)**	**DOC (mg/L)**	**POC (µg/L)**	**Ca (mg/L)**	**Mg (mg/L)**	**Alk (mg/L)**	**HCO_3^- (mg/L)**	**CO_3^{2-} (mg/L)**
Dixon Dam	April 22, 00	112	40.5	0.79	1,430	20.2	6.3	70.7	86.2	N/A
	May 10, 00	308	238	1.8	7,500	52.2	16.3	176	202	6.0
	June 3, 00	31.8	5.6	2.2	661	52.5	16.4	165	198	1.4
	June 20, 00	15.8	7.9	2.1	513	53.7	16.6	160	195	N/A
	July 12, 00	3.6	7.6	1.9	261	51.8	16.3	155	186	1.3
	Aug. 1, 00	17.1	9.5	2.4	415	49.5	14.9	146	178	N/A
Site Data	**Cond (µS/cm)**	**pH**	**TN (µg/L)**	**Chl-*a* (µg/L)**	**Water Temperature at Time of Sampling**		**24-hour Averaged Air Temperature**		**Averaged Wind Speed During Sample Period (m/s)**	
April 22, 00	161	7.2	222	0.88	2.6		13.2		N/A	
May 10, 00	387	8.4	295	N/A	6.7		6.8		N/A	
June 3, 00	394	8.3	203	0.30	9.4		11.7		2.8	
June 20, 00	383	8.2	249	0.27	11.5		11.9		N/A	
July 12, 00	377	8.3	199	0.48	12.5		15.8		2.7	
Aug. 1, 00	355	8.2	186	0.47	17.0		18.4		3.7	