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The Role of Sockeye Salmon (*Oncorhynchus nerka*) as Biological Vectors of Contaminants

by

Eva M. Krümmel

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Abstract

When considering pathways of contaminants to pristine areas, the focus has been largely on atmospheric and oceanic transfer. In this study, sediment cores were used to study a far less investigated but very effective pathway of persistent organic pollutants (POPs) to pristine ecosystems: the biotransport by migrating sockeye salmon (*Oncorhynchus nerka*). To quantify the importance of salmon as a biotransporter of contaminants, surface sediments of lakes in Alaska and British Columbia spanning a wide gradient of salmon returns (0–40,000 salmon per km^2) were analyzed. Regressions of contaminant concentrations in the surface sediments with the number of returning salmon revealed a very strong, positive relationship. Especially for the lakes that received high numbers of spawners, sockeye salmon were found to be a more important source of PCBs (Polychorinated biphenyls) than the atmosphere. Furthermore, the quality of the relationship of PCB concentration with sockeye salmon spawners was found to be best for PCB congeners that are most abundant in sockeye salmon muscle tissue. Down-core profiles were analyzed to examine if the relationship between contaminant concentrations and sockeye salmon numbers can also be found historically within a lake. To investigate this question, contaminant concentrations in the ^{210}Pb dated sediments were compared to historical sockeye salmon counts provided by authorities in Alaska and British Columbia. The results indicate that although it is possible to find the relationship between sockeye salmon spawners and contaminant concentration in down-core profiles, it is influenced by numerous factors. Such factors can arise from contaminant patterns that result from sources other than salmon, or simply very low sedimentation rates, which lead to very low resolutions in the down-core profiles.

Résumé

Lorsque les vecteurs de transport de contaminants vers des régions éloignées sont pris en compte, l'emphase est généralement placée sur les transports atmosphériques et océaniques. Dans cette étude, des carottes de sédiments furent utilisées afin d'étudier un cheminement moins étudié, mais tout aussi efficace pour le transport de polluants organiques persistants (POPs) vers des régions éloignées: le biotransport par le saumon rouge migrateur (*Oncorhynchus nerka*). Afin de quantifier l'importance du saumon comme biotransporteur de contaminants aux sédiments de surface, des lacs de l'Alaska et de la Colombie-Britannique représentant une large portée de retours de saumons (0 à 40000 saumons par km^2) furent considérés. Les régressions de concentrations de contaminants dans les sédiments de surface avec le nombre de saumons ont démontré une forte corrélation positive. Le saumon rouge s'est avéré une source de biphenyls polychlorés (BPCs) plus importante que l'atmosphère, dans les lacs accueillant un nombre élevé de saumons géniteurs. De plus, la qualité de cette corrélation était meilleure pour les congénères des BPCs retrouvés en grande quantité dans le tissu musculaire du saumon rouge. Les carottes de sédiments profonds ont aussi été analysées afin d'examiner si cette corrélation entre les concentrations de contaminants et le nombre de saumons rouges était aussi retrouvée historiquement dans les lacs. Afin d'étudier cette question, les concentrations de contaminants retrouvés dans les carottes de sédiments datées au ^{210}Pb furent comparées avec les comptes historiques de saumons rouges fournis par les autorités de l'Alaska et de la Colombie-Britannique. Même si il est possible d'identifier des corrélations entre le nombre de saumons rouges migrateurs et les concentrations de contaminants dans les carottes de sédiments en profondeur, elles ces dernières demeurent cependant influencées par de nombreux facteurs, comme res taux de sédimentation faibles pouvant causer une perte de résolution dans les carottes de sédiments en profondeur.

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Contents

List of Tables

List of Figures

Glossary

ADF&G	Alaska Department of Fish and Game
AMAP	Arctic Monitoring and Assessment Programme
ASE	Accelerated Solvent Extractor
CFCS	Constant Flux Constant Sedimentation Rate
CIC	Constant Initial Concentration
CRS	Constant Rate of Supply
DCM	Dichloromethane
DDD	Dichlorodiphenyldichloroethane
DDE	Dichlorodiphenyldichloroethylene
DDT	Dichlorodiphenyltrichloroethane
DFO	Department of Fisheries and Oceans
GC	Gas Chromatograph
GPC	Automated Gel Permeation Chromatography Column
HCB	Hexachlorobenzene
HCH	Hexachlorocyclohexane
IOMC	Inter-Organization Programme on the Sound Management of Chemicals
IUPAC	International Union of Pure and Applied Chemistry
LOI	Loss of Ignition (Organic Matter)
MDL	Method Detection Limit
NCP	Northern Contaminants Program
NIST	National Institute of Standards and Technology
OCs	Organochlorine Pesticides
OM	Organic Matter
PCBs	Polychlorinated Biphenyls
PCDD	Polychlorinated dibenzodioxin
PCDF	Polychlorinated dibenzodioxin
PECB	Pentachlorabenzene
POPs	Persistent Organic Pollutants
RD	complete set of standards
RF	Reference Material
TBB	Trichlorobenzene
TCDD	Tetrachlorodibenzodioxin
TCDF	Tetrachlorodibenzofuran

TEFs	Toxicity Equivalency Factors
TSCA	Toxic Substances Control Act
TTBB	Tetrabromobenzene
UNEP	United Nations Environmental Programme
USEPA	US Environmental Protection Agency

Chapter 1

Introduction

Since the introduction of synthetic chemicals such as DDT and PCBs at the beginning of the last century, our planet has been subject to a bombardment of ever new emerging chemicals that are meant to facilitate the human existence in this world and aid in our development. Based on the USEPA's (US Environmental Protection Agency) Toxic Substances Control Act (TSCA) Chemical Substances Inventory for 1985, more than 58,000 chemicals exist. In Canada, 23,000 chemicals are listed under the 'Domestic Substances List' (based on substances present in Canada between 1984 and 1986), of which a total of 69 have been on the 'Priority Substances List', and required toxicity testing. Of those 69 chemicals, 43 were found to be toxic and have to be regulated or further assessed. This means that 62% of the chemicals on the Priority Substances List were found to be a risk to the health of Canadians or the environment. If a similar percentage were applied for the Domestic Substances List, more than 14,000 chemicals that are in use in Canada today are toxic. This is a frightening perspective if it is considered that even chemicals that are banned in most parts of the world, such as PCBs and DDT, can still be found in substantial amounts in the environment. Furthermore, as will be described in more detail below, chemicals that are in use in other parts of the world are subject to various transport mechanisms in the environment and may be found in areas where they have never been produced or used. It is therefore not surprising that the young discipline of environmental toxicology (often also referred to as 'ecotoxicology') is a fast growing field. Environmental toxicology combines the interests of ecology (i.e., the study of interactions between organisms and their environment) and toxicology (i.e., the study of toxins and their effects on living organisms). However, environmental toxicology is not only concerned with the ecological and toxicological effects of pollutants, but also with their fate (transport, transformation and breakdown) in the environment [48]. Challenges here have been lately the establishment of trends due to a lack of time series measurements [101]. Paleolimnological approaches, in which sediment cores from lakes or oceans are utilized to establish historical records, have therefore often been used to obtain otherwise not accessible information.

This thesis integrates methods used in paleolimnology and environmental toxicology to investigate the newly discovered transport of persistent organic pollutants (POPs) by migrating Pacific salmon. The following paragraphs provide background information about persistent organic pollutants, the importance of Pacific salmon to their nursery systems, and the use of paleolimnological methods.

1.1 The history of persistent organic pollutants (POPs)

When Rachel Carson first described the detrimental impact of organochlorine pesticides on the environment in her book "Silent Spring" in 1962, she noted: "To find a diet free from DDT and related chemicals, it seems one must go to a remote and primitive land, still lacking the amenities of civilization. Such a land appears to exist, at least marginally, on the far Arctic shores of Alaska [...]. When scientists investigated the native diet of the Eskimos in this region it was found to be free from insecticides. The fresh and dried fish; the fat, oil, or meat from beaver, beluga, caribou, moose, oogruk, polar bear, and walrus [...] all had so far escaped contamination."

Twenty years later, researchers were surprised to find elevated levels of chemicals such as organochlorine pesticides and PCBs in blood and lipid tissues of Indigenous populations in northern Canada, although possible emission sources were far away [35]. It was found that the chemicals that were produced and used in temperate regions had finally found their way into the Arctic food web, with the result that the formerly pristine diet of Indigenous peoples is now described as being among the most contaminated [30]. Studies like these prompted international efforts to better control the production, use, release and trade of toxic chemicals and let to the initiation of programs such as Canada's Northern Contaminants Program (NCP), and the Arctic Monitoring and Assessment Programme (AMAP) [35]. More specifically, in 1995, the United Nations Environmental Programme (UNEP) Governing Council invited the Inter-Organization Programme on the Sound Management of Chemicals (IOMC) and other international bodies to assess 12 specific compounds, now known as the "dirty dozen" (Table 1.1, source: [74]). The resulting convention was signed in 2001 in Stockholm by 114 countries. The aim of this convention is

Table 1.1: The UNEP "Dirty Dozen"

POP	Date of Introduction	Definition and Use
Aldrin	1949	Insecticide
Chlordane	1945	Insecticide
DDT	1942	Insecticide
Dieldrin	1948	Insecticide
Endrin	1951	Rodenticide/Insecticide
Heptachlor	1948	Insecticide
Hexachlorobenzene	1945	Fungicide
Mirex	1959	Insecticide
Toxaphene	1948	Insecticide
PCBs	1929	Commercial Applications
Dioxins	1920s	Combustion Byproduct
Furans	1920s	Combustion Byproduct

to eliminate or severely restrict the production and use of certain persistent organic pollutants. The reason for this international effort can be found in the complexity of those contaminants: Persistent organic pollutants (POPs) are defined as organic compounds that resist degradation (photolytic, biological, and chemical) to a varying degree, and have a half-life of greater than eight weeks [126, 81]. The stability of the molecules is caused by aromatic structures and/or halogen (usually chlorine) substitutes, which are also responsible for their low water solubility and semi-volatile properties [126]. Because these compounds tend to be lipophilic, they accumulate in fatty tissues and thus biomagnify up the food chain. The persistence of those molecules, along with semi-volatility and high lipid solubility has resulted in the omnipresence of POPs: they have been measured in every major climatic zone and geographic sector throughout the world [126]. Exposure of living organisms to POPs can occur through diet or environment and can cause a wide range of health effects, including illness and death. Studies in the laboratory and in the field have linked POPs to endocrine disruption [120], reproductive and immune dysfunction [8], neurobehavioural disorders [76, 77, 52, 51, 129, 128] and cancer [42] in animals and/or humans. The most important groups of the POPs investigated in this study will be discussed in more detail in the following paragraphs.

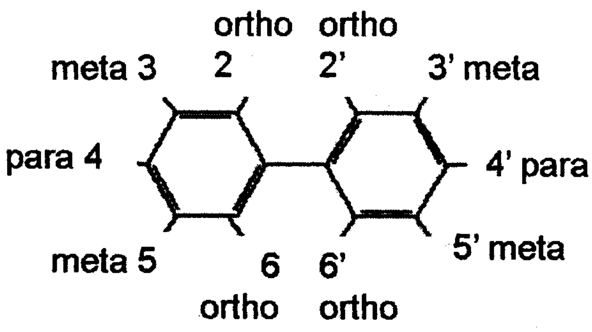

Figure 1.1: Chemical structure of PCBs, with possible chlorine substitutions numbered and labeled. Modified from [131].

1.2 Polychlorinated Biphenyls (PCBs)

PCBs are mixtures of 209 structurally similar congeners, which have been produced commercially since 1929. Their favorable properties are chemical inertness, heat resistance, non-flammability, low vapour pressure and a high dielectric constant. The industrial uses included dielectrics in transformers and large capacitors, heat transfer fluids (in heat exchangers and hydraulic fluids), organic diluents (in paints, plastics, adhesives, lubricant, sealants), pesticide extenders, flame retardants, cutting oils and as a component of carbonless copy paper [131]. PCBs were used extensively from 1930 to mid-1970, with peak production and usage in the U.S. occurring in 1970 [117]. PCBs mostly found their way into the environment through improper disposal, storage practices and accidents. Although new uses of PCBs have been banned in most countries by 1980, old uses might continue. Macdonald et al. [97] also estimate that $\sim 2*10^8$ kg are still mobile in the environment, which is approximately 35% of the initially produced amount.

PCBs have been assigned systematic numbering by the International Union of Pure and Applied Chemistry (IUPAC), which depends on chlorination of the biphenyl rings (Figure 1.1): higher numbers are associated with higher chlorination of the molecule.

The individual PCBs can be distinguished according to the quantity of chlorine substitution (monochlorobiphenyls - decachlorobiphenyls) or the location of the chlorines (ortho-, meta-, or para- substituted PCBs). Assessing the toxicity of PCBs is complicated because of the slightly different chemical and toxicolgical properties of the various congeners. The toxicology of PCBs is significantly affected by the position of chlorines and it has been found that 13 PCBs, which resemble 2,3,7,8-polychlorinated dibenzodioxin (2,3,7,8-PCDD) and 2,3,7,8-polychlorinated dibenzofurans (2,3,7,8-PCDFs)(Figure 1.2), have a higher toxicity than other PCBs [2].

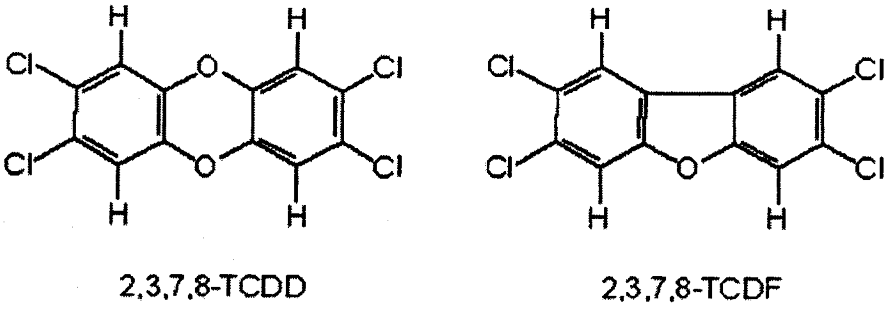

Figure 1.2: Chemical structure of the most toxic TCDDs/Fs

Thus, dioxin-like "TEFs" (toxicity equivalency factors)have been assigned to make a toxicological comparison more feasible. Examples for those PCDD/F resembling PCBs are congener 77 (position of chlorines are 3,3',4,4'), 126 (chlorine positions: 3,3',4,4',5), and 169 (chlorine positions: 3,3'4,4',5,5'). In general it can be said that the more toxic PCBs are those which have no chlorine substitutions in ortho positions. Chlorine atoms in these positions hinder the rotation of the rings and, therefore, PCBs without ortho substitution are referred to as coplanar, and the others as noncoplanar [126]. Coplanar PCBs resemble 2,3,7,8- TCDD in that they bind to the aryl hydocarbon receptor (AhR), which induces transcription of cytochrome P450 monooxygenases [131]. These enzymes are responsible for the metabolizing of xenobiotics, but in doing so they also create harmful epoxide metabolites and OH radicals, which then lead to serious damage in body tissues and can promote tumors. In accidents in Japan (1968) and Taiwan (1979) a large number of people were exposed to PCBs and PCDFs contaminated rice oil [126]. The exposure resulted in various symptoms, such as enlargement and hyper secretion of the Meibomian glands of the eyes, swelling of the eyelids and pigmentation of the nails and mucous membranes, sometimes associated with fatigue, nausea and vomiting. Symptoms extended to children born up to 7 years after maternal exposure in the Taiwan incident and included hyperpigmentation, deformed nails and natal teeth, intrauterine growth delay, poorer cognitive development, behaviroural problems and higher activity levels [71, 25]. Jacobson et al. [77] also reported prenatal exposure to PCBs to cause a poorer short term memory functioning in 4-year old children.

Concerning the chemical properties of PCBs it can be generalized that water solubility and vapour pressure decrease with increasing chlorine substitution, whereas lipid solubility increases. PCBs associate with the organic fraction of soils, sediments, and biological tissues and with the dissolved organic carbon in aquatic systems in the environment [126]. Especially the lower chlorinated PCBs volatilize from water surfaces because of their hydrophobicity, and atmospheric transport is expected to be a significant pathway for the distribution of those PCBs. The higher chlorinated PCBs are less likely to travel long distances through the atmosphere because of their low vapour pressure. Due to their lipophilic properties they bioaccumulate and concentrate readily in biota and can be transported by animal movement (see below).

1.3 Organochlorine pesticides

Pesticides have a long history in human agriculture, and with their development, usage increased substantially. The first generation of pesticides predominated from the late-1800s to the 1940s and was mostly based on inorganic compounds such as arsenic, copper and sulfur [99]. They were not widely used because of their non-target specific properties and inefficiency. Organochlorine pesticides (OCs) are the second generation of pesticides and were widely used since the 1940–50s to the present because of their low cost and high efficacy. In what follows I provide a brief overview of the OCs examined in this study.

1.3.1 DDT

The best-known OC pesticide is probably dichlorodiphenyltrichloroethane (DDT). It has two stereoisomers, o,p'-DDT, and p,p'-DDT. Their aerobic and anaerobic degradation products are dichlorodiphenyldichloroethylene (DDE) and dichlorodiphenyldichloroethane (DDD), respectively. The prominence of DDT in North America was caused by Rachel Carson's book "Silent Spring" [24], which was published in 1962 and discussed the effect of DDT on biota in the environment. In the beginning, DDT was an immense success story, which led to a mass screening of other organochlorine compounds for their potential as insecticides. Although DDT was synthesized in 1874, its insecticidal properties were not discovered until 1939 by the Swiss scientist Peter Müller. It was thought to be very safe for non-target organisms and thus widely used, for example during WWII to control typhus, which was spread by the body louse, or against malaria mosquitoes [126]. DDT was the most widely used agricultural insecticide in the world between 1946 and 1972

[95]. Peak production might have occurred in 1959 in the U.S. [117], but China continued to produce DDT until 1983, and reached peak production in 1975 and in 1980 [95]. After the publication of "Silent Spring", concern about adverse environmental effects started to grow, and severe restrictions and bans were put in place in many developed countries [126]. Nonetheless, due to lack of an alternative, DDT is still in use in several developing countries to control malaria mosquitoes.

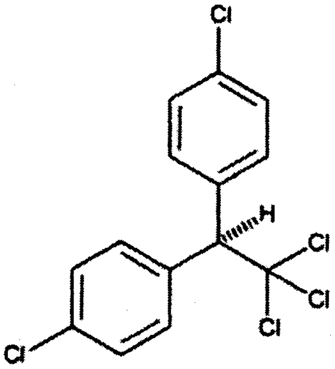

Figure 1.3: The chemical structure of DDT.

1.3.2 Chlordane and Heptachlor

Chlordane is a mixture of >140 related compounds, but most of them are only found in trace amounts. Up to 85% of technical chlordane are comprised of α- and γ- chlordane, which are stereoisomer forms. Other major consituents are chlordene, heptachlor and cis- and trans- nonachlor. Chlordane was used as an insecticide in agriculture on crops such as corn and citrus and in homes on lawns and gardens from 1946 until 1983 in the U.S. The USEPA then banned all uses except those for controlling termites, which were also banned in 1988. However, production of chlordane continues for export [47].

Heptachlor was extensively used as an insecticide in buildings and food crops up to 1970, but is also a breakdown product and component of chlordane. Heptachlor epoxide is the more toxic and persistent oxidation product of heptachlor and is formed during metabolism of heptachlor in animals and by bacteria. Although the commercial sale of heptachlor was banned by USEPA in 1988, and the commercial use is restricted to controlling of fire ants in power transformers, it is still available outside of the U.S. [47].

1.3.3 Aldrin, Dieldrin and Endrin

Aldrin and dieldrin are related insecticides (aldrin is metabolized to dieldrin by plants and animals). Both were used extensively from the 1940's to the 1970's in agriculture (e.g. on corn, cotton and potatoes) to control termites, the corn rootworm, grasshoppers and other insects. Peak usage in the U.S. occurred in 1966. The U.S. Department of Agriculture stopped the use of aldrin and dieldrin in 1970, but in 1972 until 1987 the chemicals were approved by the USEPA for killing termites [47]. All usages in the U.S. were canceled in 1989.

Endrin is a stereoisomer of dieldrin which was used as an insecticide, rodenticide and avicide on cotton, sugarcane, tobacco, grain and apple orchards beginning in 1951. Its registration in the U.S. was voluntarily canceled by the producer in 1991 because of endrin's toxicity to raptors and migratory birds, but uses may continue in other countries [47].

1.3.4 Chlorobenzenes

Chlorobenzenes were utilized as solvents in pesticide synthesis (especially in the production of DDT) or as intermediates in the manufacture of other halogenated organics [47, 102].

Pentachlorobenzene (PECB) was also used as a fungicide and a flame retardant, and in Canada it was included as an additive in dielectric fluids together with PCBs [147]. Peak production of chlorobenzenes in the U.S. took place in 1960 and has since declined considerably [47].

Hexachlorobenzene (HCB) was applied as a fungicide on seeds and grains until 1984, but it is also a byproduct of many manufacturing processes, e.g. in the production of solvents and chlorinated pesticides. It was also used in various other applications, such as a in dye manufacturing and as a wood preservative [47]. Current releases of HCB are possible due to ongoing uses in developing countries and improper storage or disposal practices [47, 36].

1.3.5 HCH

The photochlorination of benzene yields technical-grade hexachlorocyclohexane (HCH). α-HCH is the main component (60-70%) in technical HCH, which consits of a total of 8 isomers, only 5 of which are stable ($\alpha, \beta, \gamma, \delta$, and ϵ) [96]. Technical HCH is a broad-spectrum insecticide and was used extensively worldwide, but is now banned by most countries [95]. China had the highest usage of technical HCH and started producing it in 1952. The production reached maxima in 1972 and 1980, but was followed by a steep decline after HCH was banned in 1983. Although technical HCH is not being used anymore, lindane, which is almost entirely made up of γ-HCH, is still applied in many countries [96].

1.3.6 Endosulfan

Technical endosulfan consists to 94% of its two isomers, α and β endosulfan, in a 7:3 ratio. It was first introduced in the U.S. in 1954 by the company Farbwerke Hoechst A.G. Endosulfan is an insecticide currently applied on over 60 different crops, reaching from cotton and tobacco to tomatoes, lettuce and many other food crops, as well as in home gardening and for wood preservation [47].

1.3.7 Methoxychlor

Methoxychlor is structurally very similar to DDT, and was intended to replace it due to its apparent lower toxicity. It was commercially produced in the U.S. since 1946, and was available as a 'General Use Pesticide' over the counter. Methoxychlor has been applied as a pesticide and fumigant on more than 85 crops, and it was used in aerial applications on beaches, marshes, estuaries and lakes to control fly and mosquito larvae [47]. The USEPA canceled the registration of the last methoxychlor product of its major producer Kincaid in 2003 [146].

Like PCBs, OCs are chemically persistent and semi-volatile, causing their omnipresence in the environment. From the UNEP list of the dirty dozen (Table 1.1), 9 compounds are organochlorine pesticides and include aldrin, dieldrin, endrin, DDT, chlordane, heptachlor, hexachlorobenzene, mirex and toxaphene. Although their exact mode of action is often still unclear, they are known to be neurotoxins which act on the central (e.g., aldrin) or peripheral nervous system (e.g., DDT) [61]. The general effect of hyper-excitability of nerves and muscles is apparently caused by destabilization of the nerve membrane, whereby a single electrical stimulus leads to multiple uncontrolled response of poisoned nerves [61].

DDT is acutely toxic to birds and especially its metabolite dichlorodiphenyldichloroethane (DDE) is known to cause eggshell thinning through its estrogen-like behavior in the endocrine system [62]. It has been noted that several OC pesticides such as DDT, chlordane, HCB and toxaphene are able to induce immunodeficiency in a variety of wildlife species [126]. The adverse effect of OCs in wildlife is also evident by the observation that stranded beluga whales in the St. Lawrence with a high incidence of tumours also had significantly elevated levels of mirex, chlordane, toxaphene and PCBs [126]. For humans, direct pesticide handling especially in developing countries has been shown to pose the greatest risk. A study in the Philippines showed that endosulfan was the first cause of pesticide-related acute poisoning among rice farmers and mango sprayers in 1990 [126].

In the future, third generation pesticides are thus likely to be used in greater quantities. Those pesticides are mostly nitrogen- and phosphorus based, and generally have a shorter half-life and a more specific toxic mode of action than OCs [99]. Nevertheless, because of their persistence and their semi-volatile and lipophilic properties, OC pesticides will remain an important topic for years to come.

1.4 Mercury (Hg)

Although mercury is a metal, it fulfills all the prerequisites for a persistent organic pollutant, and is therefore usually included with the 'legacy' POPs listed above. Inputs of mercury to the environment can arise from both natural and anthropogenic sources [111]. Several studies suggest that total mercury in the atmosphere has increased over the last hundred years, and that those increases are related to human activities since the industrial revolution [46, 65]. Mercury is released through anthropogenic processes such as fossil fuel burning, smelting of metals (such as Zn, Cu and Pb), chlorine and pesticide production, as well as waste incineration [10]. Mercury is a very distinct element due to its numerous chemical and physical forms, which are accompanied by varying chemical and physical properties [10]. Elemental mercury (Hg^0) is volatile and therefore mostly found in the atmosphere, where it has a residence time of at least a year [14]. It is deposited by precipitation in lakes and on soil, where it binds to particles in its ionic form (Hg^{2+}). Once it reaches the soil or sediments, the inorganic mercury is processed to methyl mercury (CH_3Hg^+ or MeHg) by sulphate-reducing bacteria. Methyl mercury is resistant to degradation, and is therefore persistent in the environment [10]. Methyl mercury is not only the most toxic form of mercury, it also binds to protein in body-tissue and therefore bioaccumulates and biomagnifies in living organisms very effectively. Most affected are predators: a given concentration of methyl mercury in water will be 10,000 times higher in predatory fish and even 500,000 times higher in top predators like marine mammals [149, 94]. Once in the body, methyl mercury is readily transported through the circulatory system into liver, kidneys and even the central nervous system due to its ability to cross the blood-brain barrier [121, 3]. There it destroys cells and causes brain and nerve damage [121].

Even though global emissions of mercury have been declining recently, levels in Arctic biota are currently increasing [101]. So far, possible mechanisms are attributed to a warming of the Arctic which causes higher amounts of melt water and runoff to reach underneath the ice cover, where gaseous mercury evasion is blocked off [101]. Likewise, climate warming is suspected to be responsible for increased mercury fluxes to sediments in Arctic lakes, although the mechanism here is more likely related to higher lake productivity [101].

Similar to PCBs and OC pesticides, mercury has been shown to be subject to transport by migrating salmon [152, 132], and albeit limited measurements have been conducted in this study, its importance should not be underestimated.

1.5 Transport pathways of persistent organic pollutants

When considering pathways of contaminants to pristine areas, the focus has been largely on atmospheric transfer [41]. Wania and Mackay [148] proposed a model, which explained how POPs reach remote areas such as the Arctic, where those chemicals have never been used. They hypothesized that POPs evaporate in warmer regions of use, travel a certain distance through the atmosphere and subsequently condense and deposit in colder regions. Depending on volatility of the compounds the rate of transport will vary: highly volatile compounds remain airborne longer and migrate faster, less volatile POPs will tend to partition more readily into water or snow and precipitate sooner onto soil, vegetation, and watersheds. The authors propose a process analogous to a gas chromatographic separation, with a varying composition of contaminant mixtures along a temperature or latitudinal gradient. A concentration profile of a compound in the environment then depends on its volatility: immobile POPs will have the highest concentration near their point of release and will decline with distance, mobile POPs, however, will show the opposite pattern. These phenomena are indeed observed for mobile compounds such as HCB [23, 138] and HCHs [138]. PCBs are ideal for the detection of latitudal, compositional changes in contaminant mixtures, because they are used as combinations of various congeners with different chemical properties. Examinations of Canadian lake sediments from a wider latitudinal scale found that high arctic lakes had greater proportions of the more volatile congeners [114]. Because the migration of the chemicals takes time, a time delay in deposition of the contaminants would be expected, and this delay depends on their mobility. A temporal study of different semi-volatile organochlorine pesticides in snow and ice samples from Snow Dome glacier in Alberta found a delayed deposition of those compounds. DDT and dieldrin, whose use was widely restricted in the mid 70's, reached maximum concentrations in the mid to late 80's in the glacier at Snow Dome [32]. The authors from this study hypothesized that meltwater from glaciers will release significant quantities of organochlorine pesticides into aquatic ecosystems for decades to come. Indeed, a study by Blais et al. [13] found that the dominant sources of persistent organic pollutants in glacier fed mountain lakes are glacially derived tributary inputs. Thus the atmosphere has become a major source of contaminants, which, combined with the food-web, produces high exposure in top predators. The impact of contaminants transported via the atmosphere can therefore measure up to or even exceed that of anthropogenic point sources [99, 112].

A far less explored and less obvious contaminant pathway is the transport of POPs by migrating animals. First observations of salmon acting as a source of PCBs and DDT to tributaries of Lake Michigan were reported by Merna in 1986 [106]. A similar mechanism was confirmed in a second study regarding the biotransport of mirex by salmonids [137]. However, it was not until ~10 years later that the possibility of salmon acting as a significant transporter of contaminants was considered again by Ewald et al. [41]. They investigated the pollutant transport in a population of sockeye salmon (*Onchorynchus nerka*) in Copper River, Alaska. In the study, the influence of the biotransported POPs was examined by comparing pollutant composition and levels in atmospheric deposition as well as in two different populations of arctic grayling (*Thymallus arcticus*), a resident fish. One grayling population was from a lake that received pollutants by atmospheric deposition only; the other population was from a nearby lake that received sockeye salmon spawners. They found that the grayling in the lake, which received salmon, exceeded concentrations of POPs by more then two-fold compared to those of the graylings in the non-salmon lake. The authors concluded that biotransport of PCBs and DDT by salmon had a far greater influence on lake biota than atmospheric input.

The biotransport by salmon is not restricted to organochlorine contaminants: Zhang et al. [152] estimated that 21 kg of methyl mercury were transported to Bristol Bay river ecosystems by Pacific salmon over a 20-year period.

Similarly, transport of contaminants is not restricted to Pacific salmon. Several studies have now demonstrated that birds can act as a significant transporter of contaminants, e.g. Arctic seabirds [16, 40]. Even though the transport mechanism is different in that the birds deliver contaminants and nutrients through their droppings, it is still very effective due to the sheer number of birds which might reach around 300,000 individuals per colony, with an estimated 3.8 million kg of guano (Blais et al., submitted).

Although the contaminant pathway of animal migration is much smaller in scale compared to atmospheric transport or that of oceanic currents, it is very effective through the direct nature of the delivery, which focuses contaminants from a vast area (e.g., the ocean) into a rather small vicinity (e.g., a lake). It also enables the direct uptake of contaminants into local food-webs, without intermediate processes such as adsorption to particles and deposition [41]. Even more important might be the possibility that non-persistent pollutants, which are not subject to abiotic transportation, can be transferred by biovectors, as was found for chlorinated fatty acids transported by salmon [110].

1.6 Influence of the sockeye salmon life cycle on nursery lakes

Five species of Pacific salmon (genus *Oncorhynchus*) reproduce in North America: sockeye (*O. nerka*), pink (*O. gorbuscha*), chum (*O. keta*), chinook (*O. tshawytscha*) and coho (*O. kisutch*) [57]. Their complex life cycle has not only made them culturally and economically important to humans along the North American west coast, it also provides a continuous linkage between the marine environment and oligotrophic nursery lakes. Since the different Pacific salmon species vary in their life history patterns, and sockeye salmon are more closely connected to lakes as nursery freshwaters for various reasons, the latter will be discussed in more detail in the following section.

Sockeye salmon spawn in gravel beds associated with lakes, and the juveniles rear in their nursery lakes for 1 to 3 years, before they migrate to the ocean [20]. They spend 1 to 4 years in the ocean, where they feed on euphausids, amphipods, small fish, and squid, and accumulate up to 99% of their total body weight [20, 105]. As soon as they return to their freshwater nursery streams, sockeye salmon stop feeding, and also undergo dramatic changes in shape and color. After reaching their nursery lakes, they spawn and, as with all Pacific salmon species, die shortly after. Studies found a large increase in the abundance of dissolved nutrients following the massive die-off of spawned-out Pacific salmon [19, 125, 144] and it has been suggested that this source of nutrients is significant for the mostly oligotrophic lakes [87, 85, 115]. Several studies have examined the nutrient input into freshwater systems by Pacific salmon using stable isotopes, especially ^{15}N. Marine nitrogen is enriched in ^{15}N relative to terrestrial and freshwater nitrogen [83] and is also higher in organisms that feed at higher trophic levels [29, 119, 22]. Isotopic compositions of natural materials can be measured with a mass spectrometer, and are expressed as a per mil deviation from a recognized isotope standard [119]. In the case of nitrogen, the ratio is measured relative to atmospheric nitrogen:

$$\delta^{15}N = \frac{^{15}N/^{14}NSample -^{15}N/^{14}NAir}{^{15}N/^{14}NAir} \tag{1.1}$$

A study by Mathisen et al. [105] examined the importance of Pacific salmon derived nitrogen to a nursery lake by analyzing different trophic levels for their ^{15}N values. They found a shift in $^{15}N/^{14}N$ isotope ratios between trophic levels in a salmon and a control lake of +1 to +3 mil. It was concluded that migratory salmon play a major role in the nitrogen dynamics of the examined lake system. This nutrient cycle is especially important for sockeye salmon, since it is the only Pacific salmon with a juvenile stage that is dependent on its nursery lake habitat and a forage base of zooplankton [84].

It was observed previously that Pacific salmon stocks are declining [122]. In an more specific estimate including 41 of 52 Pacific Ocean ecoregions, Augerot [7] assessed the status of a total of 7,519 salmon stocks. Of those, 23% were found to be at moderate or high risk, and an estimated 278 stocks are now extinct [7]. Several authors assume that declining salmon stocks could be partly due to reduced nutrient loadings simply caused by lower numbers of spawners [84, 79, 104]. However, it was recently suggested that theoretically, if spawner densities were very low, smolts could export more nutrients than their parents imported. More specifically, Moore and Schindler [109] estimated that the emigration from sockeye salmon smolts removed an average of 16% of the phosphorus and 12% of the nitrogen that their parents imported, but maximum values of up to 65% of phosphorus and 47% of nitrogen were reached. Other reasons for declining escapement numbers (fish that return to their nursery systems to spawn) such as overfishing, habitat degradation, construction of dams and climate change have been widely discussed. Persistent organic pollutants could also play a very important role in decreasing escapement numbers. Salmon use their sense of smell to find their way back into their nursery systems, and the substances that guide their migration have been shown to include volatile organic compounds [60]. Laws [93] assumes that organic pollutants could alter the characteristic smell of the water in such a way that salmon would be unable to identify their home stream. Another study by Arkoosh et al. [5] found that juvenile Chinook salmon from polluted estuaries are immunosuppressed and are more susceptible to disease than salmon from less-polluted water. They concluded that anthropogenic contaminants could significantly shift the balance between salmon survival and mortality due to disease. Thus, the complex life history of Pacific Salmon, which developed over thousands of years to ensure survival of the young, might now also pose a risk to these populations.

1.7 The use of biological indicators in lake sediments

Lakes often act as a sink of materials draining from the watershed and airshed. They collect and integrate local and regional environmental signals, which then are stored chronologically in the sediments. Undisturbed sediments can usually be found in the deep portion of the lake, and have long been used as a reliable indicator of past environmental change [139, 99]. Sediment cores can be taken from a boat or through ice with a messenger-operated gravity corer, and sectioned in fine intervals. These intervals can then be dated and used for further examinations. Various biological indicators can provide information about the lakes' history. Diatom frustules, exoskeletons of invertebrates, pollen grains and spores, charcoal, ash (tephra) particles etc. can be used to determine trends in terrestrial and aquatic vegetation succession and provide information about pH of lake water, nutritional lake status, forest fires, volcano eruptions and much more [139]. Several studies were able to track past nutrient dynamics in salmon nursery lakes using stable isotopes ratios [44, 43, 105] with diatom and invertebrate indicators in lake sediments [44, 43]. As explained above, salmon systems are significantly enriched in ^{15}N relative to non-salmon systems. The ^{15}N ratios fluctuate with time depending on numbers of returning salmon, and this information is stored in sediments [43]. Diatoms consist of thousands of different species, which vary in shape and size of their siliceous call walls (frustules) as well as their nutrient and pH preferences. They respond to environmental shifts very quickly and their frustules preserve well in sedimentary deposits [139]. Thus, Finney et al. [44, 43] used a combination of ^{15}N ratios and diatoms to reconstruct past sockeye salmon abundances over 300 and 2,200 years in Alaskan lakes. They were able to show that decadal-scale variability in salmon is not unique to the 20th century, and is caused in part by climate-related factors. So far, contaminant-related changes have not been investigated, although especially the above discussed POPs are very well suited for preservation in sediments. Because of their persistence and hydrophobicity, they attach to organic materials and accumulate in the sediments [17, 99]. Together with other biological indicators and stable isotope ratios, this data can provide more information about missing links between salmon escapement fluxes and anthropogenic influences.

1.8 Research objectives

This study is based on the hypothesis that Pacific salmon act as a transport mechanism of contaminants. Even though the occurrence of biotransport of contaminants by salmon has been suggested previously, its importance and magnitude compared to other transport mechanisms remained uncertain. The general objective of this study was therefore to determine if a relationship can be found between salmon escapement in west-coast nursery lakes and the deposition of persistent organic pollutants to sediments of these lakes, as would be predicted by the hypothesis. Two different approaches were taken:

1. The spatial relationship between the number of salmon that return to their nursery lakes to spawn and the surface sediment contaminant loading of those lakes was examined. Since the lakes are located in the same geographic area, it was assumed that they receive the same amount of atmospheric contaminant deposition, and that the main difference regarding the contaminant input between the lakes is given by the number of salmon spawners.

2. Because lake sediments represent natural environmental archives and allow inferences about the history of contaminant deposition and past sockeye salmon trends, the temporal changes of POP deposition were investigated. Down-core profiles of contaminants were compared to those of δ^{15}N values, as well as actual numbers of salmon that returned to spawn (counts of spawners were provided by the Department of Fisheries and Oceans as well as the Alaska Department of Fish and Game). Provided that other sources of contaminants to nursery lakes were negligible in the past, higher contaminant fluxes during periods of higher salmon returns in dated sediment cores can be expected.

Chapter 2

Methods

2.1 Site Location

Geographical coordinates and physical characteristics of the lakes sampled in this study are presented in Table 2.1; the locations of the lakes are displayed in Figure 2.1. Some details about the lakes will be provided in the following sections.

2.1.1 Kodiak Island, Alaska

The lakes on Kodiak Island were in the most remote location, and only accessible by floatplane. Five lakes were sampled there and include Frazer, Karluk, Red, Spiridon and Upper Olga.

Frazer Lake is situated between Red Lake (to the west) and Karluk Lake (to the east) on the southwest side of Kodiak Island. Frazer was naturally not a salmon receiving lake, because a 10-m high waterfall prevented the salmon from entering the system [56]. Beginning in 1951 sockeye salmon eggs were deposited in the lake, and fish ladders were introduced in 1962 and 1979, the latter of which caused the steep increase of sockeye salmon escapement to the lake, which peaked in the early 1980's. Additionally, Frazer Lake was fertilized from 1988 to 1992 to boost productivity and aid in smolt survival [56].

Karluk Lake is the largest of the Kodiak lakes analyzed in this study (Table 2.1). Karluk Lake is located close to Frazer Lake and also shares many similarities, but unlike Frazer Lake, Karluk is naturally a salmon receiving lake. Karluk Lake has been fertilized from 1986 to 1990, and was also stocked with sockeye salmon eggs and fry from 1978 to 1984 [56].

Red Lake is one of the smallest lake in this study (Table 2.1), and receives the most sockeye salmon spawners on a per area basis.

Spiridon was included as a control lake because it does not receive any salmon spawners. Although the lake is stocked with salmon fry to enhance to productivity of the system, no spawners can return due to a waterfall at the outlet of the lake [38].

Upper Olga Lake is part of the South Olga Lakes system on Kodiak Island, which is composed of two lakes: Lower and Upper Olga Lake. On some maps the lakes are identified as Upper Station, which refers to an old research station that used to be at the outlet of Lower Olga Lake (Nicholas Sagalkin, ADF&G, personal communication). Upper Olga has a surface area of 7.9 km^2 and has a maximum depth of 70 m (Table 2.1). It is connected to Lower Olga Lake, which is smaller (4.4 km^2) and shallow (mean depth of 2 m), and feeds into Olga Bay, on the southwest side of Kodiak Island.

2.1.2 Bristol Bay, Alaska

Three of the sockeye salmon nursery lakes included in this study were sampled on the Alaskan mainland, in the Bristol Bay area, southwestern Alaska: Becharof, Iliamna and Upper Ugashik. All lakes are located in National Wildlife Refuges, with very little development, and only two inter-community road systems [92]. Most supplies for the little communities in the area are brought in by air transport or over water. All of the lakes are a very important part of the salmon production systems in the area.

Iliamna is the largest sockeye salmon producing lake in the world, and the largest lake in Alaska. Salmon enter the lake via the Kvichak River, and a counting station for salmon is placed at the outlet of the lake [105].

South of Iliamna lies Becharof Lake, which is the second largest lake in Alaska and is located in the Egegik River watershed.

Upper Ugashik Lake is situated south of Becharof Lake. It is separated from Lower Ugashik Lake by the Ugashik Narrows. The lakes are drained by Ugashik River, which has a seasonally staffed salmon-counting weir at the outlet of Lower Ugashik Lake.

2.1.3 British Columbia

Kinaskan Lake is located in northern B.C., close to Highway 37. The south end of Kinaskan Lake is situated within Kinaskan Lake Provincial Park and has a small campground, but otherwise no development. Kinaskan Lake was chosen as a control lake since it does not receive any salmon, and because of its close proximity to Meziadin Lake and

Alaska. It will be used to evaluate the atmospheric impact of POPs that can also be expected for the salmon lakes.

Meziadin Lake is situated in northern B.C. on Highway 37, approximately 160 km south of Kinaskan. Similar to Kinaskan, Meziadin has its own small Provincial Park, and a campground is located at its north end. There is slightly more development in this area compared to Kinaskan Lake, as Meziadin Lake has some houses and cottages on its east shore. The town of Stewart is 65 km to the west. Meziadin Lake has a fishway which was built in 1966 to allow salmon to bypass a series of waterfalls called the 'Victoria Falls'. Since the existence of the fishway an observatory station is operated by DFO personnel during the summer, who carry out daily counts of returning salmon and also take biological measurements. Therefore, Meziadin salmon spawners numbers can be assumed to be very reliable and accurate.

Shuswap Lake is located in central B.C., close to several small cities such as Kamloops and Salmon Arm, and has small towns on its shores, which are connected by small roads. The shape of Shuswap Lake resembles that of a chromosome, it has 4 arms which are joined more or less in the middle. It is the largest of the B.C. lakes sampled in this study (Table 2.1). There are several Provincial Parks with campgrounds around Shuswap Lake, and Highway 1 runs along the southern shores of two arms. The coring location was at the southwest end of Shuswap Lake, close to the inflow of Adams River.

Bowron Lake is the smallest of the B.C. lakes investigated (Table 2.1). The lake is situated close to the Cariboo Mountains, in Bowron Lake Provincial Park. The watershed area is less developed compared to that of Shuswap Lake. There are no towns directly on the lake, only one campground is located on the northeast side. Road access is limited to the northern side of the lake.

Quesnel Lake is slightly smaller than Shuswap (Table 2.1), but with a maximum depth of 530 m the deepest of all the lakes sampled in this study, and among the 15 deepest lakes world-wide [81]. It is located approximately 70 km south of Bowron Lake, close to the Cariboo Mountains Provincial Park. Two small towns are relatively close to the lake, but road access is very limited.

Fraser Lake is situated on Highway 16, approximately 120 km west of the City of Prince George. There are several small towns on the south shore, and Beaumont Provincial Park with a campground on the north shore of the lake.

Table 2.1: Site location, coring years and morphometric characteristics of the lakes sampled.

Site	Location	Lat(N)	Long(W)	Coring Year	Lake Area (km^2)[a]	Lake Depth max. (m)[a]	Watershed Area (km^2)[a]
Becharof	Alaska Mainland	58°03’	156°15’	1995	1172	181	3379.45
Iliamna	Alaska Mainland	59°30’	155°	1997	2662	393	16888.15
Upper Ugashik	Alaska Mainland	57°24’	157°18’	1995	212.71	~150	1291.74
Frazer	Kodiak Island	57°16’	154°08’	1998, 2002	16.6	59	181
Karluk	Kodiak Island	57°25’	154°05’	1995, 2002	39.4	126	282
Red	Kodiak Island	57°15’	154°20’	1998, 2002	8.4	48	43.8
Spiridon	Kodiak Island	57°72’	153°68’	2002	9.2	80	> 60
Upper Olga	Kodiak Island	57°04’	154°10’	1998, 2002	7.9	70	40.1
Fraser	B.C.	54°05’	124°45’	2001	54	30.5	6268
Bowron	B.C.	53°13’	121°22’	2002	10.2	63.4	3403
Shuswap	B.C.	51°00’	119°00’	2002	330	162	16221
Quesnel	B.C.	52°30’	121°00’	2002	270	530	5930
Meziadin	B.C.	56°03’	129°16’	2003	34	133	530
Kinaskan	B.C.	57°35’	130°08’	2003	28.7	N/D[b]	1251

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[a] Information was taken from refs [50, 69, 91, 85, 90, 141].

[b] No data was available.

2.2 Sampling

Sampling occurred in several different years:

In 1995–1998 three sockeye salmon nursery lakes were sampled on the Alaskan mainland (Becharof, Upper Ugashik and Iliamna lakes) and four sockeye salmon nursery lakes on Kodiak Island (Frazer, Karluk, Red and Upper Olga lakes).

In 2002 four lakes on Kodiak Island were re-sampled (Frazer, Karluk, Red and Upper Olga lakes) and one control lake was added (Spiridon Lake, where sockeye salmon cannot return to spawn due to a waterfall).

A total of 6 lakes were sampled from 2001 to 2003 in British Columbia. In 2001 and 2002 cores were taken in central B.C., from salmon receiving lakes Fraser, Bowron, Quesnel and Shuswap. In 2003 two cores were taken from Meziadin and Kinaskan lakes, which are located in northern British Columbia, very close to the Alaskan border (Figure 2.1). Kinaskan Lake, which does not receive anadromous salmon, serves as a second control. In 2002 and 2003, sockeye salmon were also collected from the salmon nursery lakes listed above.

Sediments were collected using corers designed specifically for high-resolution paleolimnological work [53]. Since lakes in Alaska were accessible only by float plane, whereas BC lakes were accessible by a small boat, different corers were used in the two regions. The corer used for BC lakes had an inner diameter of 9.5 cm and was lowered using an electric winch, which made it easier to collect cores from greater lake depths. The heavier weight of this corer also allowed for extraction of longer cores. In Alaska a smaller, hand-operated corer was used (inner diameter: 7.6 cm). Using bathymetric and topographical maps when available, cores were collected from deep parts of the lakes, with low gradients and well away from river mouths or deltas. Cores were extruded on site at fine intervals, the sediment slices were placed in WhirlPak® bags, sealed and frozen immediately. In the lab, wet sediments were weighed for bulk density and water content calculations. Subsamples of selected intervals were freeze-dried for dating and isotope analysis, whereas wet sediments were used for contaminant analysis.

2.3 Contaminant Extraction: Sediments

Wet sediment samples were centrifuged at 2500 rpm to remove excess water and mixed with Hydromatrix®, which was pre-cleaned with petroleum ether. This mixture was spiked with surrogate recovery standards of PCB 30 and PCB 204, as well as OCs 1,3,5-

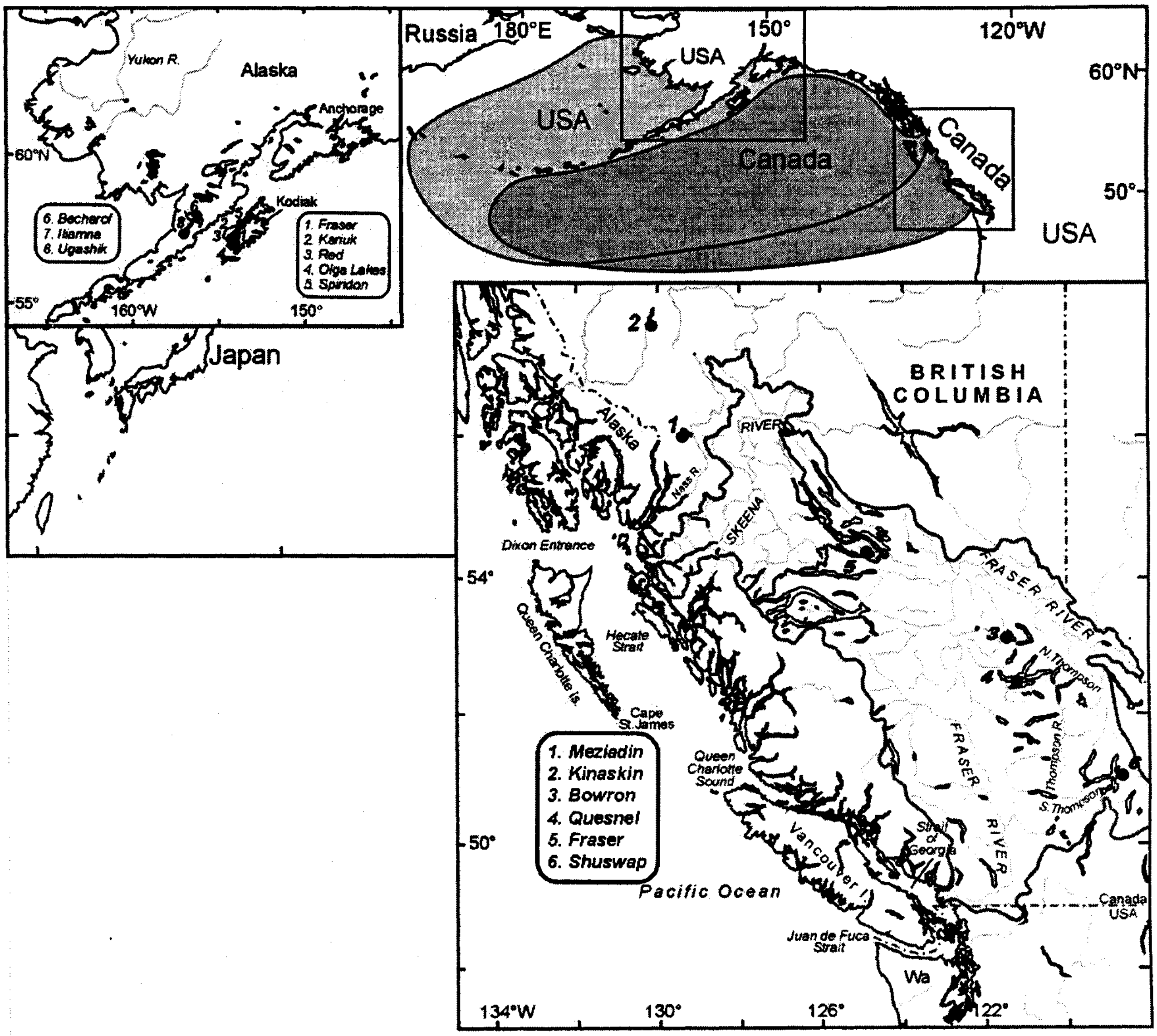

Figure 2.1: Map of Alaska and British Columbia showing the lakes sampled in this study. The shaded areas indicate the sockeye salmon migration range in the Pacific Ocean (modified from [11]).

TBB, 1,2,4,5-TTBB, δ-HCH and endrin ketone, and extracted in an accelerated solvent extractor (ASE, Dionex). The samples underwent two extractions at 2000 PSI and 100 °C each, first with acetone/hexane, followed by dichloromethane (DCM). The two extracts were then combined for liquid-liquid extraction, and dried over sodium sulphate. The resulting volume of 150 ml was reduced to 1 ml in a TurboVap (at 14 psi using ultra high purity nitrogen gas, and 35 °C waterbath temperature) and exchanged into iso-octane. Cleanup and fractionation was accomplished by passing the extracts through a chromatographic column packed with 8 g of activated silica gel and 1 g sodium sulphate. A first extract (A-fraction) was eluted with 50 ml of hexane and contained all the PCBs and some percentages of a few OC pesticides. The second extract (B-fraction) was eluted with 80 ml of 1:1 hexane and dichloromethane, and contained the remaining OC pesticides. Sulphur was removed in a last step using elemental mercury (Sigma-Aldrich, 99.9995% purity, A.C.C. grade). All extracts were then evaporated down to 200 μl in iso-octane and a known concentration of Mirex was added as an internal standard. All solvents used were Omnisolv® high-purity grade from VWR (Mississauga, ON).

2.4 Contaminant Extraction: Fish

Approximately 8 g of salmon white muscle with skin were ground up in pre-cleaned Hydromatrix®. The mixture was packed into ASE cells, spiked and extracted using the ASE as described above for the sediments, except that in these extractions, DCM was used first, and then hexane. The two extracts were combined and dried over sodium sulphate. Lipids were then removed by running the extract through an automated gel permeation chromatography column (GPC Autoprep 1002A, Analytical Bio-Chemistry Laboratories, Inc.) with a 45:55 mixture of DCM and hexane. Fractionation was accomplished by using a similar method as described for the sediments. As a last step, samples were evaporated in iso-octane down to 500 μl, to which a known concentration of Mirex was added. To determine lipid content, approximately 3 g of muscle tissue with skin were extracted with DCM using the ASE. The extract was then left in the fume hood to evaporate, followed by oven-drying at 60 °C for ~ 8 hrs to ensure complete dryness and finally the weight was recorded and subtracted from initial weight measurements.

2.5 Quality Control

Reference material (RF), consisting of the National Institute of Standards and Technology (NIST) 1944 River Sediment was run with each batch of sediment samples. A complete set of standards (RDs), and method blanks were also routinely analyzed with every sample batch.

RDs and surrogate recovery standards can be used to estimate the recoveries of the analyzed compounds. Method blanks represent the background contamination associated with the analytical process, which is then removed from the samples by subtracting the method blank from the sample value. Method blanks are also used to determine method detection limits (MDLs) by calculating the standard deviation of the averaged method blanks and multiplying it by 2 (which achieves a 95% confidence level).

Since the laboratory was moved three times during the course of this study, which can be expected to affect the background contamination, MDLs were calculated separately for the three locations.

RF material is usually used to estimate the precision and accuracy of the analytical process. However, the NIST contained very high concentrations of contaminants compared to the samples in this study, and compounds frequently shifted during the chromatographic process, which made it difficult or even impossible to analyze the compounds accurately. Therefore, less than half of the initially included RFs could be used for the final data analysis.

Tables with recoveries, MDLs and RF values can be found in the Appendix, Section A.1.

2.6 Analytical Techniques

PCBs and organochlorine (OC) pesticides were analyzed on a Hewlett-Packard 6890 series II gas chromatograph with a ^{63}Ni micro electron-capture detector, using splitless injection with an inlet temperature of 250 °C. One microlitre of extract was separated on a 30 m x 0.25 mm (0.25 μm film) DB-5MS column (J&W Scientific) using Helium carrier gas at 3.1 ml/min on constant flow. The oven ramping program is as follows: initial temperature of 80 °C held for 2 minutes, climbing to 110 °C at 10 °C per minute, then to 280 °C at 3 °C per minute and held for 5 minutes. The detector temperature was at 350 °C using constant column flow plus makeup nitrogen gas at 60 psi. The instrument was calibrated using a 5-point calibration curve, using standard concentrations ranging from

1.9 to 530 pg/μl with a correlation coefficient of ≥ 0.99. Chromatographic peaks were interpreted using HP Chemstation software (Rev. A.06.03, Hewlett-Packard, Palo Alto, CA). Compounds were identified by running sets of standards with known concentrations and comparing their retention times with those of the sample compounds. Concentrations of the sample compounds were calculated by taking the ratio of their peak areas and the peak area of an internal standard (Mirex), which was added prior to injecting the sample.

From the 209 PCB congeners in the standard mixture, usually about 100 peaks could be obtained, with small differences depending on GC maintenance. They appear in the following order (IUPAC number): 1, 3, 4-10, 7-9, 6, 8-5, 19, 30, 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, 48-47, 44, 59-42, 40, 100, 63, 74, 70-76-98, 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, 146, 153-132-105, 141-179, 137, 176, 138-163, 158, 129, 178, 175, 187-182, 183, 128, 167, 185, 174, 177, 202-171-156, 173, 157-200, 204, 172, 197, 180, 193, 191, 199, 170-190, 198, 201, 203-196, 189, 208-195, 207, 194, 205, 206, 209.

From the OC pesticides standard mixture, not all compounds could always be reliably identified. Difficulties arose from high background noise in the chromatograms and co-elution of pesticides in the A-fractions with PCBs. The OC pesticides analyzed for included: pentachlorobenzene (PECB), α-hexachlorocyclohexane (α-HCH), hexachlorobenzene (HCB), γ-hexachlorocyclohexane ("Lindane", γ-HCH), heptachlor, aldrin, heptachlor epoxide, γ-chlordane, α-endosulfan, α-chlordane, dieldrin, p,p'-dichlorodiphenyldichloroethylene (p,p'-DDE), endrin, β-endosulfan, p,p'-dichlorodiphenyldichloroethane (p,p'-DDD), o,p'-dichlorodiphenyltrichloroethane (o,p'-DDT), methoxychlor.

Frequently co-eluting compounds in fraction A were p,p'-DDE and PCB 85, as well as o,p'-DDT and PCBs 114-134-131.

2.7 Isotope Analysis

For elemental and isotopic analysis of nitrogen and carbon, between 5 to 20 mg of freeze-dried sediments were weighed into small tin boats and combusted at over 1000 ^{o}C in an Atomic Absorption Spectrometer (AAS). The thereby produced gases of N^2, SO^2 and CO^2 were separated by megabore packed columns and analyzed for total percentages of nitrogen, sulphur and carbon. About 3% of the gases were passed on to an Isotope-Ratio Mass Spectrometer (IRMS) and analyzed for isotope ratios. Isotopic compositions are expressed as δ values, which are measured as parts per thousand differences from a standard [119]:

$$\delta \mathrm{X} = \left[\left(\frac{\mathrm{R_{sample}}}{\mathrm{R_{standard}}} \right) - 1 \right] * 10^3, \tag{2.1}$$

where X = the heavy isotope of C or N (^{13}C or ^{15}N),
and R = the corresponding ratio ($\frac{^{13}C}{^{12}C}$, or $\frac{^{15}N}{^{14}N}$).

The standard for nitrogen is the nitrogen gas in air, and the standard for carbon is carbon in the PeeDee limestone. Per definition, standard δ values are 0‰.

To ensure that only organic carbon is analyzed for δ^{13}C, samples are often acidified to remove inorganic carbon prior to isotope analysis. When applicable, samples were acidified via fumigation, whereby sediments were placed in silver boats and moistened with HPLC grade water. Samples were then placed in a dessicator along with an open beaker full of concentrated HCl for 24 hours. After fumigation, the sediments were dried at 60 °C and analyzed as described above.

2.8 Loss of Ignition (LOI)

Methods of LOI were based on a study by Heiri et al. [63]. In order to determine organic matter content in the sediments, freeze-dried sediments were placed in crucibles and exposed to 550 °C for four hours in the furnace. The samples were allowed to cool to room temperature in a dessicator to avoid water uptake through condensation, and differences in weight were recorded gravimetrically. Organic matter content (OM) was calculated by:

$$\mathrm{OM} = \left[\frac{(\mathrm{DW_{FD}} - \mathrm{DW_{550}})}{\mathrm{DW_{FD}}} \right] * 100, \tag{2.2}$$

where $\mathrm{DW_{FD}}$ = weight of freeze-dried sediments (g),
and $\mathrm{DW_{550}}$ = weight of sediments after combustion at 550 °C (g).

Carbonate content in the sediments was determined in a second step, whereby the sediments, which were previously burned at 550 °C, were placed in the furnace again and burned at 950 °C for two hours. After cooling in the dessicator, weights were recorded and carbonate content calculated by:

$$\text{Carbonate} = \left[\frac{(\text{DW}_{550} - \text{DW}_{950})}{\text{DW}_{\text{FD}}}\right] * 100, \tag{2.3}$$

where DW_{FD} = weight of freeze-dried sediments (g),
and DW_{550} = weight of sediments after combustion at 550 °C (g),
and DW_{950} = weight of sediments after combustion at 950 °C (g).

Chapter 3

Dating of lake sediments

3.1 Introduction

In order to connect certain events in sediments with the known history of the area (e.g. comparing known escapement numbers with ^{15}N profiles or PCB profiles down-core), it is necessary to date the sediments. This chapter will give a brief overview of dating methods commonly used in paleolimnology, with a focus on ^{210}Pb dating, which was used in this study. The important equations used in the dating process will be presented, as well as dating results from the sediment cores described in Chapter 2.

3.1.1 Radioisotopes used for dating of sediments

Naturally occurring radioisotopes currently provide the best means for dating [139]. ^{14}C (carbon) is commonly used to date organic deposits that are 500–40,000 years old. ^{14}C forms in the atmosphere because of cosmic-ray bombardment of ^{14}N (nitrogen). The radioactive ^{14}C decays to its stable form at an estimated decay half-life of 5730 +/- 40 years [139]. Organisms take up ^{14}C until equilibrium with the environment (atmosphere) is reached. As soon as the organism dies, no new ^{14}C will be incorporated and the remaining ^{14}C will decay in accordance with the radioactive law. But because of the long half-life, ^{14}C dating cannot be used to attain recent time-scales. This, however, can be accomplished by ^{210}Pb (lead)-dating, a methodology developed by Krishnaswami [86]. ^{210}Pb is a naturally occurring daughter-isotope of ^{238}U (uranium). ^{238}U decays in the environment with a half-life of $4.51*10^9$ years to ^{226}Ra (radium). ^{226}Ra (half-life of 1602 years) then decays to the gaseous ^{222}Rn (radon). A fraction of the ^{222}Rn atoms escape to the atmosphere. ^{222}Rn has a very short half-life of 3.82 days and decays further through a series of short-lived radionuclides to ^{210}Pb (see Figure 3.1). Because of the escapement of ^{222}Rn, there are two sources of ^{210}Pb in a given sediment sample: supported ^{210}Pb originates from in situ decay of ^{226}Ra. Unsupported ^{210}Pb stems from decaying ^{222}Rn in the atmosphere with subsequent precipitation or dry deposition on land or water column. From the latter, ^{210}Pb is scavenged and deposited with the sediments [4]. There, the unsupported ^{210}Pb decays according to the radioactive decay law with a half-life of 22.26 years and can be used to date sediment from recent times to 150 years back. ^{210}Pb in sediments is commonly measured through its gamma ray emissions, or by alpha spectrometry. In alpha spectrometry ^{210}Pb is determined by alpha radiation emitted by ^{210}Po, which is a granddaughter product of ^{210}Pb. A disadvantage in this measurement is the long storage time required before the sediments can be processed. Because ^{210}Po can only be used as a measure of ^{210}Pb when the two are in steady state, and its half-life is relatively long (138 days), samples have to be stored for several months [4]. Gamma spectrometry does not require such a long storage time, and also allows for measurement of other useful radioisotopes. For example, ^{226}Ra is measured and used to estimate the supported ^{210}Pb, which should be in steady state with ^{226}Ra, provided the sediments are stored for 3 weeks in sealed containers to avoid ^{222}Rn escapement. The supported ^{210}Pb can then be subtracted from the total ^{210}Pb to obtain unsupported ^{210}Pb [12].

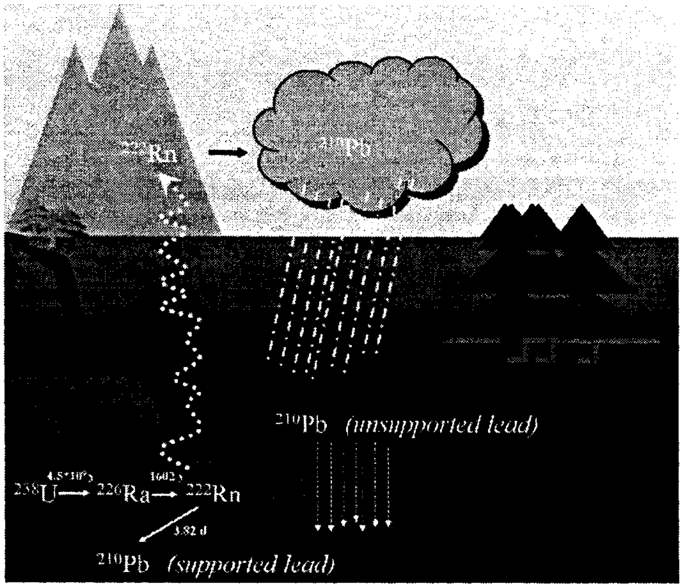

Figure 3.1: Sources of ^{210}Pb into lake sediments. See text for detailed explanation.

A number of assumptions have to be met to obtain reliable dates when using simple dating models [86]:

- The rate of ^{210}Pb deposition is constant through time
- Unsupported ^{210}Pb-activity derives only from atmospheric fallout
- Sediments were undisturbed (no mixing of the surficial sediment has occurred)
- ^{210}Pb decays exponentially according to the radioactive decay law

Several models now exist which differ slightly in the conditions that have to be fulfilled for the models to be valid. For example, some of the models can incorporate mixing events, but generally the assumptions listed above have to be met to ensure reliable dating. A more detailed description of the three prevalent dating models will be given in the following sections.

3.1.2 ^{210}Pb dating models

CFCS model

Since ^{210}Pb deposition on longer time-scales (a year or more) is relatively uniform, the 'simple' dating model can be assumed for lakes where erosive processes in the catchment are steady and which have a constant productivity [127]. The age t (y) of sediments can be determined by dividing the cumulative dry mass (g cm^{-2}) at depth m by the dry mass sedimentation rate r (g cm^{-2} y^{-1})[4]:

$$t = \frac{m}{r} \tag{3.1}$$

For the simple dating model to be valid, the sedimentation rate r and the supply of unsupported ^{210}Pb have to remain constant. For this reason, the model was also named the 'constant flux constant sedimentation rate' (CFCS) model [116]. In that model, the unsupported ^{210}Pb activity C (Bq Kg^{-1}) at depth m can be described by:

$$C(m) = C(0)e^{-\frac{\lambda m}{r}}, \tag{3.2}$$

where λ = the radioactive decay constant of ^{210}Pb = 0.03114 y^{-1}
and C(0) = the unsupported ^{210}Pb activity at the surface of the core.

Thus, when ^{210}Pb activity is plotted against depth or cumulative dry mass, it will show a uniform exponential decline. However, many lakes may experience variation in sediment accumulation because of erosion, glacial input, or changes in lake productivity. This will lead to a dilution in unsupported ^{210}Pb activity in the sediments due to increased sedimentation rates, and ^{210}Pb activity might not display a uniform exponential decline with depth. Other reasons for a non-uniform exponential decline might include a change of ^{210}Pb supply to the sediments, variations in sediment focusing rates, or mixing. In lakes with varying sedimentation rates, usually either one of two models can be used:

CRS model

The CRS (constant rate of supply) model assumes that unsupported ^{210}Pb is delivered to the sediments at a constant rate, but might experience variations in the sediments due to changing sediment accumulation rates. That means, a ^{210}Pb-profile versus depth in the sediment core can deviate from an exponential curve since changes in sedimentation rate would dilute or concentrate the ^{210}Pb in the sediment [15]. Because of these changes of the initial ^{210}Pb concentrations, the dates of the sediments are calculated from the distribution of ^{210}Pb in the sediment record, rather than the actual ^{210}Pb concentrations [4]:

$$A = A(0)e^{-\lambda t}, \tag{3.3}$$

where A = ^{210}Pb inventory (Bq m^{-2})
and A(0) = A at time zero.

A and A(0) are calculated by numerical integration of the concentration versus depth profile [4].

The age of the sediments can then be obtained by:

$$t = \frac{1}{\lambda} ln \left(\frac{A(0)}{A} \right) \tag{3.4}$$

CIC model

The CIC (constant initial concentration) model assumes that the initial ^{210}Pb is constant, but varies with the sedimentation rate. Thus, the ^{210}Pb supply in a given sediment profile will increase or decrease proportionally to the sediment flux. Since the unsupported ^{210}Pb is constant, the following equation describes the ^{210}Pb concentration C at depth m:

$$C(m) = C(0)e^{-\lambda t}, \tag{3.5}$$

where C(0) = C at a depth of zero.
The age of the sediments is then obtained by:

$$t = \frac{1}{\lambda} ln \left(\frac{C(0)}{C} \right) \tag{3.6}$$

The CIC model might be valid when the main delivery of ^{210}Pb to the sediments is not via the atmosphere but through in-wash from the catchment (allochthonous particle input), or when increased sedimentation of autochthonous material leads to increased sequestering of ^{210}Pb from the water to the sediments [116]. Nevertheless, the initial ^{210}Pb concentration has to remain constant, and therefore a steady decline in a ^{210}Pb-profile versus depth would be expected [15].

However, neither of the models is valid if ^{210}Pb supply rates have changed. If mixing of the surficial sediments occurred, but the ^{210}Pb flux remained constant, modified CFCS (provided that also the sedimentation rate stayed constant) or CRS models may still give valid chronologies [116].

3.1.3 Independent markers for model testing

Independent validations of the obtained dates are recommended to achieve a high confidence in the results [4], and several techniques can be used. In order to validate dates for the last 30–40 years artificial radionuclides, specifically ^{137}Cs (caesium), are the most commonly used. ^{137}Cs was released on a large global scale through atmospheric nuclear weapons testing from the United States and Russia during the cold war. In most sediments in the Northern Hemisphere there is an onset in 1954, with a peak identifying the 1963 depth [4, 139, 15]. In regions close to the Chernobyl accident (former Soviet Union, Europe, and Turkey), a second ^{137}Cs peak identifies the 1986 depth. Care has to be taken if there are ^{210}Pb and ^{137}Cs discrepancies. Blais et al. [15] found that hard water (mineral rich, conductivity $> 75\ \mu$S cm^{-1}) sediments trap ^{137}Cs more effectively than soft water (organic rich, conductivity $< 25\ \mu$S cm^{-1}) sediments. Thus, molecular diffusion of ^{137}Cs in soft water sediments can occur.

A method to identify depths in the mid to late 1800's (time of European settlement) is the Ambrosia pollen horizon. Widespread deforestation during that time increased the abundance of Ambrosia (ragweed), which resulted in an increase of Ambrosia pollen in sediments to as much as 10% of the total pollen [15]. Other changes in pollen assemblage are also used and can be found in [139] and references therein.

Because volcano eruptions lead to a wide deposition of very distinct ash (tephra) layers, those also can be used to link a specific sediment interval to a recorded event. The term "tephrochronolgy" describes the use and identification of tephra, a wide range of airborne pyroclastic material ejected during a volcanic eruption, in sediments as a geochronological technique [145]. Provided that a lake is located sufficiently proximal to an eruption site, the sediments can contain several distinct tephra horizons that can be observed by the naked eye. Varying grain size, colour and thickness of the different tephra layers can be used for identification, and a large number of laboratory techniques are available to identify micro-tephra particles. Since "micro-tephra horizons" or "cryptotephra" have a wide range of morphological types, they can be easily matched up with a certain volcano eruption-event [145].

3.1.4 Sedimentation rates and focusing factors

Dating by the radioisotope ^{210}Pb is particularly helpful in contaminant work because it can be used to obtain information about factors such as sedimentation rates, sediment focusing and physical mixing that might influence contaminant accumulation in sediments. Most studies concerned with the distribution of contaminants in sediments report not only concentrations, but also fluxes of the contaminants in sediments. Contaminant fluxes are calculated by multiplying the contaminant concentration with the sedimentation rate, and thus can account for dilution or concentration due to variable sedimentation rates. Depending on which dating model is used, sedimentation rates can differ throughout a core (CRS and CIC models) or stay constant (CFCS model). If sedimentation rates have not been constant within a core, it might be advisable to correct for varying sedimentation rates when contaminant changes are followed through time (as in the case with down-core profiles). Even in the case of constant sedimentation rates corrections might be necessary when contaminant concentrations in different lakes are being compared. However, sedimentation rates calculated by ^{210}Pb dating includes all particles sequestered into the sediments from the water column, but does not at a given site differentiate enhanced sediment accumulation due to focusing. Sediment focusing is a gravitationally forced process in which resuspended sediments tend to move from shallow to deeper parts of the basin through water motion [28]. Therefore, in cases where such lateral movement of sediment to the coring site in the basin has occurred, an additional focus correction might be required, e.g. if comparisons between different coring locations are warranted. Focusing factors are calculated by dividing the ^{210}Pb inventory of a given core by the expected atmospheric ^{210}Pb flux. Details regarding the calculations of sedimentation rates and focusing factors are given below.

3.2 Methods

The sediment cores taken in 2001–2003 were dated using the dating software described below, whereas sediment cores from 1995–1998 were obtained from Bruce Finney (University of Alaska Fairbanks), who also collected the ^{210}Pb data for those cores. Since the sediments from 1995–98 were mostly used for surface sediment analysis, only the CFCS model was applied to these data, to obtain sedimentation rates and focusing factors.

The sediments that were subsampled for dating were freeze dried, ground to a fine powder, and filled into centrifuge tubes (8.4 cm high and 1.5 cm outer diameter) up to a height of $\sim$ 2 cm (between 1–2 g). After the sediments were settled, the tubes were sealed with epoxy and allowed to reach radioactive equilibration for 3 weeks before counting on a digital, high purity germanium spectrometer (DSPec, Ortec). The detector consists of a germanium crystal with lithium diffused electrodes. The volume between the electrodes is depleted, and a high voltage produces an active field across the whole region. When there is photon interaction through emission of γ-rays from a sample, electrons and holes are produced, which are swept toward the positive and negative electrodes. Upon reaching the electrodes, a charge-sensitive preamplifier converts the charge into a voltage pulse that is proportional to the energy deposited. A thick lead shield prevents background radiation from reaching the germanium crystal, which is also consistently cooled with liquid nitrogen to prevent spontaneous electron movement.

Since sediment samples usually have very low radiation, they have to be counted for at least 23 h (82800 sec) to get a strong enough signal. Due to background noise, a minimum of 400–500 counts per radioisotope have been found to be necessary to obtain a good signal to noise ratio. The resulting spectrum files show ^{210}Pb activity with a peak at 46.5 keV, and ^{137}Cs at 662 keV. ^{226}Ra activity is determined by γ-ray emissions of its daughter isotope ^{214}Pb at 295 and 352 keV. The activity A of a sample is calculated by

[4]:

$$A = \frac{N}{\epsilon Y t}, \tag{3.7}$$

where N is the number of counts in the peak,
ϵ the detector efficiency,
Y the yield of photons of an energy E, and t the count time.

The spectrum files were processed by a DOS-based software program developed and provided by Peter Appleby (University of Liverpool, U.K.), which included calculations for efficiency and corrections for self absorption [4]. Absolute efficiency calculations are necessary because detectors can vary substantially in the effectiveness of photon detection at different energies. Efficiency calibrations are thus essential when supported ^{210}Pb concentrations are determined by emissions of the parent radioisotope ^{226}Ra. Self absorption happens at low energy γ-ray emissions within a sample and is dependent on the density of the sample.
Sediment bulk densities were calculated following equations found in [59]:

$$\rho_w = \frac{100 * \rho_m}{100 + (W + IG^0)(\rho_m - 1)}, \tag{3.8}$$

where ρ_w = wet weight bulk density in g cm^{-3},
ρ_m = density of solid particles in g cm^{-3},
W = water content in percent,
IG^0 = loss on ignition expressed in percent of total wet weight.

A default value of 2.6 for ρ_m can be used as a general rule of thumb for bulk density determinations [59]. Equation 3.8 can then be written as:

$$\rho_w = \frac{260}{100 + 1.60(W + IG^0)} \tag{3.9}$$

Dry bulk density was subsequently determined by:

$$\rho = \left(\frac{1 - W}{100}\right) \div \left(\frac{1}{\rho_w} - \frac{W}{100}\right) \tag{3.10}$$

All sediment cores were dated using the three models described above (CFCS, CRS and CIC), and the best model was determined by comparing the dating results to the occurrence of the ^{137}Cs peak in the down-core profile. In a previous study, which tested the accuracy of the different models in lake sediment cores, the CRS model consistently provided the best fit [15]. Similar results were found in this study, although in many cores sedimentation rates did not change substantially through time, and therefore the CFCS model often achieved comparable results. Most calculations, including those for cummulative dry mass, radioisotope activities, CRS and CIC models, were done within the dating software. Only the pertinent equations will be discussed here, for a detailed description see [4]. Also, since the CIC model was not applicable for the cores dated in this study, only CFCS and CRS models will be described in more detail below.

Cumulative dry mass calculations

Since not all core sections were measured, a mid-point procedure utilizing the trapezium rule was applied. The cumulative mass m_n above depth x_n can be estimated with:

$$m_n = m_{n-1} + \frac{1}{2}(s_n + s_{n-1})(x_n - x_{n-1}), \qquad (3.11)$$

where s_n to s_{n-1} are dry bulk densities, and x_n to x_{n-1} denote the mid-points of sections.

Cumulative unsupported ^{210}Pb calculations

If cumulative dry mass was measured in more intervals than those that have been measured for ^{210}Pb, a subset of the above determined cumulative dry masses m_n to m_{n-1} was used. Although a similar procedure as above using the trapezium rule can be employed, a more accurate approach is an equation that assumes that ^{210}Pb concentrations between data points vary exponentially:

$$\hat{A}_n = \hat{A}_{n-1} + \frac{C_{n-1} - C_n}{ln(C_{n-1}/C_n)}(m_n - m_{n-1}), \qquad (3.12)$$

where $\hat{A}_n$ is the cumulative unsupported ^{210}Pb above depth x_n or cumulative dry mass m_n, and C_n to C_{n-1} the unsupported ^{210}Pb concentrations corrected for mass.

CFCS model calculations

Calculations based on the CFCS model were computed from total ^{210}Pb activities and cumulative dry mass by fitting an exponential curve through the data using the following equation:

$$C_{tot}(t) = C_{uns}e^{-\lambda t} + C_{sup}(1 - e^{-\lambda t}), \tag{3.13}$$

where C_{tot} is the total ^{210}Pb activity, λ is the radioactive decay constant for ^{210}Pb, C_{sup} is the ^{210}Pb activity supported by the parent radioisotope ^{226}Ra, and C_{uns} is the unsupported ^{210}Pb activity (slightly modified from [4]).

The first term on the right side, $C_{uns}e^{-\lambda t}$, expresses the unsupported ^{210}Pb activity from time of burial to the deepest sample counted. The second term, $C_{sup}(1 - e^{-\lambda t})$, depicts the supported ^{210}Pb activity, which exhibits an exponential rise from zero to C_{sup}, since supported ^{210}Pb is generated in the sediments by decay of the parent radioisotope ^{226}Ra.
A program for the fitting exercise was written using MATLAB, which also calculated sedimentation rate, the unsupported ^{210}Pb inventory, and CFCS dates. Figure 3.2 shows the ^{210}Pb profile of Bowron Lake plotted against cumulative dry mass as an example (Figures B.1 and B.2 in the Appendix show profiles of all lakes). The fitted equation is shown, as well as the parameters fitted. The sedimentation rate (r) was calculated by multiplying parameter 1 (p_1) with λ (the ^{210}Pb decay constant). The ^{210}Pb inventory was calculated by multiplying p_1 with p_2. CFCS dates were calculated by simply dividing cumulative dry mass by the sedimentation rate (see equation 3.1). Sediment focusing factors were estimated by dividing ^{210}Pb inventories of a given sediment core by the expected atmospheric ^{210}Pb flux (1042 Bq $cm^{-2}yr^{-1}$, value based on [108]).

To ensure a reliable dating process, it is of crucial importance to determine the right concentration of supported ^{210}Pb in the core. As mentioned above, the method of choice is usually to establish the concentration of ^{226}Ra, which, when in equilibrium, should be commensurate with the supported ^{210}Pb. However, in two out of 12 cores equilibrium conditions were not reached, although total ^{210}Pb activities clearly reached background concentrations (see Figure B.3 in the Appedix for plots of the radioisotopes in the cores from 2001–2003). The most likely cause for this is ^{222}Rn escapement from the samples. In those circumstances the above described fitting process was used to establish the supported ^{210}Pb activity, which is given by the fitted parameter p_3.

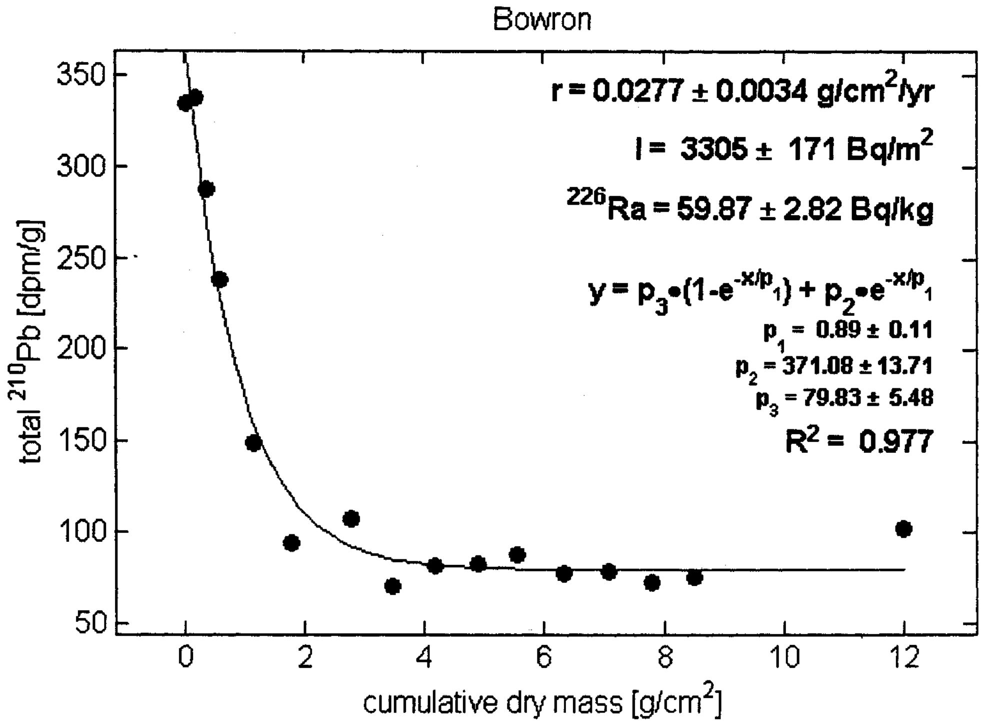

Figure 3.2: Fitting of the CFCS model through total ^{210}Pb activity against cumulative dry mass in Bowron Lake. The fitted parameters (p_1, p_2, p_3) are used to calculate the ^{210}Pb inventory (I) and sedimentation rate (r). The average of ^{226}Ra is also given. For details see text.

An example is Bowron Lake, as shown in Figure 3.2, where the displayed average ^{226}Ra value is 20 Bq kg^{-1} smaller than the fitted supported ^{210}Pb value, although total ^{210}Pb has reached background concentrations at a cumulative dry mass of around 4 g cm^{-2}.

In four other cases, the core was not quite long enough to reach background concentrations of ^{210}Pb, and p_3 was set at a fixed value (then named a_1), which was determined by the average ^{226}Ra value found in the core. Figure 3.3 shows this calculation in the example of Red Lake.

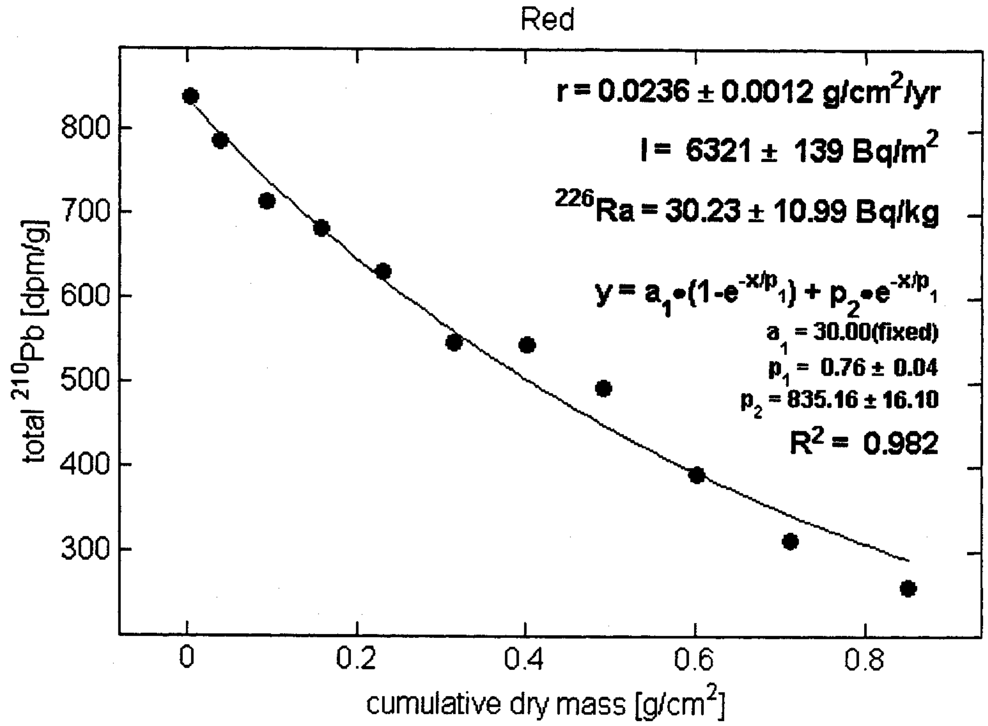

Figure 3.3: Fitting of the CFCS model through total ^{210}Pb activity and cumulative dry mass in Red Lake. The core did not reach background ^{210}Pb concentrations, thus the value for p_3 (here a_1) was set according to the average value of ^{226}Ra.

CRS model calculations

CRS model calculations are based on the unsupported ^{210}Pb inventory, as shown in equation 3.3. Here, the unsupported ^{210}Pb inventory A is defined as

$$A = A(0) - \hat{A}, \tag{3.14}$$

where A(0) = total ^{210}Pb inventory, and $\hat{A}$ = supported ^{210}Pb inventory.

Just as the case with the CFCS model (or any other ^{210}Pb dating model for that matter), it is important to have a reliable measure of the supported ^{210}Pb, because erroneous values can lead to substantial inaccuracies in the dating [4]. When reference dates such as reliable ^{137}Cs peaks are found at or above the ^{210}Pb dating horizon, they can be used to adjust erroneous dating chronologies. The ^{210}Pb inventory below the dated reference level, A_{ref}, is determined by:

$$A_{ref} = \frac{\hat{A}_{ref}}{e^{\lambda t_{ref}} - 1}, \tag{3.15}$$

where $\hat{A}_{ref}$ is the unsupported ^{210}Pb inventory above the reference level, and t_{ref} is the age of the reference level.

Dry mass sedimentation rate r at time t can be calculated using the equation:

$$r = \frac{\lambda A}{C}, \tag{3.16}$$

where C denotes ^{210}Pb activity, A the unsupported ^{210}Pb inventory, and λ is the ^{210}Pb decay constant.

The dating program also calculates standard errors for the CRS model. Not all details are given here, for a complete description see [4].

The standard error of the ^{210}Pb inventory is calculated as:

$$\sigma^2_{\Delta \hat{A}_n} = (\sigma^2_{C_n} + p^2 C_n^2)(m_n - m_{n-1})^2, \tag{3.17}$$

where p is a constant percentage error in dry mass increments (7%).

The standard error of the CRS model dates is calculated with the equation:

$$\sigma_t = \frac{1}{\lambda}\left[\left(\frac{\sigma_{A(0)}}{A(0)}\right)^2 + \left(1 - \frac{2A}{A(0)}\right)\left(\frac{\sigma_A}{A}\right)^2\right]^{1/2}. \tag{3.18}$$

The relative standard error in the sedimentation rate r is given by the equation:

$$\frac{\sigma_r}{r} = \left[\left(\frac{\sigma_A}{A}\right)^2 + \left(1 - \frac{\Delta A}{A}\right)\left(\frac{\sigma_C}{C}\right)^2\right]^{1/2}, \tag{3.19}$$

where ΔA is the cumulative inventory increment that is next to the deepest data point.

3.3 Results and Discussion

Table 3.1 summarizes the results of the unsupported ^{210}Pb inventory, sedimentation rates and focusing factors for the sediment cores listed in Chapter 2. Sedimentation rates span a range from 0.004 g cm^{-2} yr^{-1} for Fraser core 1, to 0.27 g cm^{-2} yr^{-1} for Meziadin. Most lakes had sedimentation rates within the range of 0.01 – 0.04 g cm^{-2} yr^{-1}, only two lakes have sedimentation rates below 0.01 g cm^{-2} yr^{-1}, Fraser Lake and Iliamna Lake. In Fraser Lake there are striking differences between core 1 and core 2. All values for Fraser Lake core 1 are much lower compared to core 2. Especially the focusing factor close to zero in core 1 might indicate that we failed to core the depositional basin in this part of the lake.

The other lake with a sedimentation rate below 0.01 g cm^{-2} yr^{-1}, Iliamna, is an Alaskan mainland lake with a large surface area (2662 km^2) and a very large watershed (16,888 km^2, Table 2.1). The lake is not glacier-fed and receives low organic input from the scarcely vegetated catchment.

The high sedimentation rate of Meziadin Lake is most likely caused by glacial flour input. Gilbert and Butler [50] reported sedimentation rates between 0.04 g g cm^{-2} yr^{-1} and 7.3 g cm^{-2} yr^{-1} for Meziadin Lake with higher values near the glacial inflow.

For Upper Olga (1998, Table 2.1) only surface sediments were available, and it is thus not included in this table.

For Spiridon Lake, only a very short, angled core could be obtained, which provided a poor basis for ^{210}Pb dating. The sedimentation rate for Spiridon Lake was determined using an ash layer at a depth of 4–5 cm, which was ~1 cm thick and corresponds to the eruption of the volcano Novarupta-Katmai in 1912 [70]. The ash layer was validated by microscopic analysis, which confirmed the presence of volcanic glass.

Table 3.1: Summary of results for the unsupported ^{210}Pb inventories, sedimentation rates and focusing factors for all the lakes.

Lakes	^{210}Pb inventory (Bq m^{-2})	Sedimentation rate (g cm^{-2} yr^{-1})	Focusing factor
Cored 2001–03			
Fraser Core 1	240 ± 51	0.0040 ± 0.0013	0.2
Fraser Core 2	2981 ± 921	0.1521 ± 0.0679	2.9
Bowron	3305 ± 171	0.0277 ± 0.0034	3.2
Quesnel	3544 ± 99	0.0140 ± 0.0007	3.4
Shuswap	4363 ± 1147	0.0616 ± 0.0233	4.2
Kinaskan	1943 ± 238	0.0272 ± 0.005	1.9
Meziadin	11528 ± 3088	0.27 ± 0.12	11.1
Spiridon	N/A	0.03	N/A
Frazer	4759 ± 799	0.0173 ± 0.0042	4.6
Upper Olga	2900 ± 375	0.0103 ± 0.0020	2.8
Karluk	5113 ± 363	0.0196 ± 0.0024	4.9
Red	6321 ± 139	0.0236 ± 0.0012	6.1
Cored 1995–98			
Becharof	3607 ± 287	0.0379 ± 0.0040	3.5
Iliamna	1792 ± 100	0.0079 ± 0.0007	1.7
Upper Ugashik	9245 ± 100	0.0697 ± 0.0116	8.9
Frazer	6396 ± 311	0.0244 ± 0.0029	6.1
Karluk	2519 ± 117	0.0112 ± 0.0010	2.4
Red	4552 ± 219	0.0159 ± 0.0011	4.4

Conductivity measurements, ^{226}Ra average, and the results for estimated supported ^{210}Pb values for lakes cored in 2001–2003 are summarized in Table 3.2. All of these cores were dated using the CRS model, and conductivity measurements are an important indicator for the reliability of the independent marker ^{137}Cs, which is used to validate or, if necessary, adjust the CRS model. The conductivity of Fraser Lake was not measured when the core was taken, and the value displayed is an average value based on measurements of the Department of Fisheries and Oceans (DFO) taken in 1992/93. The conductivity values of all lakes are above the critical value of 25 μS cm^{-1}, which indicates that the mineral content of the lakes was high enough to ensure a stable ^{137}Cs peak in the sediments [15]. Thus, ^{137}Cs was used as an independent marker to validate or adjust dates obtained from CRS models. It should be noted, however, that conductivity values at the time of sampling do not necessarily represent conductivity values of the past, particularly during the 1960's, when the ^{137}Cs fallout occurred. The possibility of some movement of ^{137}Cs in the porewater can therefore not be completely ruled out, which will most likely result in a broadening of the ^{137}Cs peak and will be discussed further when the CRS model results are presented.

The ^{226}Ra average varies between the cores from ~14 Bq kg^{-1} for Upper Olga up to nearly 60 Bq kg^{-1} for Bowron Lake (Table 3.2). As mentioned above, the supported ^{210}Pb value (estimated through the curve-fitting process) and the ^{226}Ra average should be virtually the same, if equilibrium conditions were reached. This is the case for Quesnel, Shuswap, Kinaskan and Meziadin (within error bars). Fraser core 1 and Bowron were already discussed earlier, both cores did not equilibrate although background ^{210}Pb concentrations were reached. The most likely reason for this is ^{222}Rn escapement from the samples. In the case of Fraser core 2, equilibrium was reached, but ^{226}Ra values exceed those of the estimated ^{210}Pb slightly. In this core, sedimentation rates were fairly high and variable, and ^{210}Pb in the samples relatively low, which probably resulted in a smaller signal to noise ratio and made it more difficult to detect especially the low concentrations accurately.

The last four cores listed in Table 3.2 were too short, and although equilibrium was almost reached in three of the cores (see Figure B.3 in the Appendix), there were not enough values in equilibrium conditions to enable the program to calculate accurate values for supported ^{210}Pb. This is reflected by the high standard errors, which exceed the values in all four cases. In these cores the parameter 3 in equation 3.13 was set to the ^{226}Ra average value (see Methods and Figure 3.2 and 3.3).

The dating model results with regards to the independent marker ^{137}Cs are summa-

Table 3.2: Conductivity, ^{226}Ra average, and supported ^{210}Pb values (estimated through the curve-fitting process) for the lakes cored in 2001–03.

Lakes	Conductivity (μS cm^{-1})	^{226}Ra average (Bq kg^{-1})	Estimated supported ^{210}Pb (Bq m^{-2})
Cored 2001–03			
Fraser Core 1	88	24.02 ± 4.32	48.01 ± 4.85
Fraser Core 2	88	27.40 ± 2.26	17.98 ± 5.67
Bowron	72.3	59.87 ± 2.82	79.83 ± 5.48
Quesnel	100.5	59.09 ± 3.12	54.67 ± 5.66
Shuswap	89.4	53.55 ± 2.29	62.38 ± 11.38
Kinaskan	300	22.3 ± 1.7	23.33 ± 3.30
Meziadin	99.5	40.8 ± 2.0	35.72 ± 5.37
Frazer	40.2	22.4 ± 4.6	82.69 ± 104.19[a]
Upper Olga	40.6	13.6 ± 6.7	-24.78 ± 93.42[a]
Karluk	51.3	31.9 ± 6.7	-248.68 ± 288.41[a]
Red	54.2	30.2 ± 11	-592.06 ± 597.87[a]

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[a] value set to ^{226}Ra average

rized in Table 3.3 below, as well as in Figures B.5–B.4 in the Appendix. In Table 3.3 the depth of the ^{137}Cs peak is given for the lakes cored in 2001–2003, as well as the depth interval in each dating model that corresponds to the year 1963, in which the ^{137}Cs peak should occur. It should be noted that the precision of the results depends on the spacing between measured intervals, which was at irregular distances and could lie between 1 and 5 centimeters. Therefore, the error of the ^{137}Cs peak depth was set to the furthest half slice width for each core.

A precise dating process is especially difficult when sedimentation rates are very low. For the first lake listed in Table 3.3, Fraser Lake core 1, which also had the lowest sedimentation rate, ^{210}Pb inventory, and focusing factor (see Table 3.1), the CFCS model returned the year 1969 at 1.25 cm, and 1921 at 2.25 cm. Additionally, the ^{137}Cs is difficult to interpret, because the maximum concentration was found directly at the core surface. The dating values reflect the low ^{210}Pb inventory and sedimentation rates, as total ^{210}Pb reaches background concentration at a depth of 3.25 cm, which results in a date of 1868 in the CFCS model. Other lakes that have a relatively rapid decline of ^{210}Pb, are Quesnel, Bowron and Upper Olga. The implications for paleolimnological contaminant work are apparent. Because the contaminants of interest in this study were only used starting in 1930, with peak usage in the 1960's, the resolution of complex trends in those cores will be poor.

Table 3.3: Depth of ^{137}Cs peak compared to depths in which the year 1963 occurred in the CFCS, CRS and CRS models, and the best model fit for the lakes cored in 2001–2003.

Lakes	^{137}Cs peak depth (cm)	1963 depth CFCS	1963 depth CRS	1963 depth CIC	Model chosen
Cored 2001–03					
Fraser Core 1	0.25 ± 0.5	1.25 - 2.25	0.25 - 1.25	inconclusive	CRS
Fraser Core 2	7.25 ± 1	12.25 - 14.25	6.75	3.5 + 3.75	CRS
Bowron	3.25 ± 1	3.25 - 5.25	3.25 - 5.25	inconclusive	CRS/CFCS
Quesnel	1.35 ± 0.7	1.35 - 2.7	1.35 - 2.7	1.35 - 2.7	CRS
Shuswap	10.25 ± 2.5	5.25 - 6.25	6.25	inconclusive	CRS
Kinaskan	4.25 ± 0.5	3.25	4.25 - 5.25	inconclusive	CRS
Meziadin	17.25 ± 1.5	17.25 - 20.25	11.75 - 15.25	inconclusive	adj. CRS /CFCS
Frazer	6.25 ± 0.5[a]	5.25 - 6.25[b]	6.25 - 7.25	inconclusive	CRS/CFCS
Upper Olga	2.25 ± 0.5	3.25 - 4.25[b]	3.25	3.25 - 3.5	CRS
Karluk	6.25 ± 0.5	7.25 - 8.25[b]	6.75	7.5 - 7.75	CRS
Red	8.25 ± 0.5	> 10.75[b]	9.75	> 10.75	adj. CRS

[a] corrected for sedimentation rate
[b] model with fixed p3

In general, agreement between ^{137}Cs peaks and age in the CRS and CFCS models is very good, and either one or both of the models were found to be the best fit. The CIC model often returned inconsistent dates, by going up and down in time as depth increased (see Appendix Figures B.5 – B.4). In two cases the CRS model had to be adjusted to achieve a better fit (Table 3.3, last column). In some lakes, the ^{137}Cs peak was relatively flat or of irregular shape, which made it difficult to determine a reliable maximum depth (see Figure B.3 in the Appendix). In the case of Frazer Lake, correcting the ^{137}Cs for sedimentation rate resulted in a distinct maximum at 6.25 cm, which also was in very good accordance with the CRS model. For Shuswap and Upper Olga, the ^{137}Cs peak had a very broad shape, which might indicate some ^{137}Cs movement in the core. This possibility is supported for Shuswap Lake by past conductivity data which was made available by the Department of Fisheries and Oceans in British Columbia. The data showed that conductivity was very close to and even below 25 μS cm^{-1} for some time in 1988. Although more recent values indicate much higher conductivities, it is uncertain what the lakes condition was during the 1960's, since no data was available for that time. We also do not have any historical data for Upper Olga Lake. Since the difference between the depth of the ^{137}Cs peak and the 1963 depth in the CRS model was not very large in Upper Olga, no adjustment was performed. For Shuswap Lake, adjusting the CRS model to the location of the ^{137}Cs peak returned the year of 1963 at a depth of 7.25 cm, and 1961 at 10.25 cm. This result is still within error bars of the previous, not adjusted dates (1963 at depth 6.25 cm and 1956 at 10.25 cm, with standard errors of 5 years, also see Figure B.7 in the Appendix). Because there is some uncertainty associated with the ^{137}Cs peak in this core, and the adjusted and unadjusted CRS model results were within standard errors of each other, the unadjusted CRS model was chosen.

Similar to earlier studies (e.g. [12]), it was found that dating errors for the CRS model increased non-linearly with the data (Figure B.5 – B.4). The reason is the exponential decline of ^{210}Pb in the sediments: The dating process involves a logarithmic transformation of the ^{210}Pb concentration to linearly declining years. In the error propagation, errors are inflated as the exponentially declining ^{210}Pb concentrations approach zero, and the linear transformed years approach infinity. However, in this study even greater depths returned relatively small errors, with Meziadin Lake having the maximum error of 35 years at a depth of 20.25 cm in the unadjusted CRS model. In this case, adjusting the CRS model to the ^{137}Cs peak in the core greatly reduced the error which then only reached a maximum of 6 years for the depth of 20.25 cm.

3.4 Conclusions

The total ^{210}Pb profiles from six cores taken in 1995–1998 and eleven cores taken in 2001–2003 showed the expected exponential decline with cumulative dry mass/depth. Almost all cores fitted with the CFCS dating model displayed an R^2 of 0.8 and higher, suggesting that the dating model assumptions such as a constant ^{210}Pb deposition through time and no occurrence of mixing in the sediments were met. However, four of the cores from 2002 did not reach background ^{210}Pb concentrations, and supported ^{210}Pb had to be inferred from the average value of ^{226}Ra.

Eleven cores taken in 2001–2003 were dated using CFCS, CRS and CIC models, and the independent marker ^{137}Cs was used to identify the best fitting dating model. ^{137}Cs peaks were clearly defined in eight of the eleven cores, and the generally undisturbed ^{137}Cs profiles confirmed that sediment mixing was negligible at the coring sites. However, in Frazer Lake a correction for sedimentation rate was necessary to determine the ^{137}Cs maximum depth. In the cores from Shuswap and Upper Olga the ^{137}Cs had apparently moved, as the peak was broad in both cores, and the maximum was not distinct. Therefore, the unadjusted CRS model was chosen for both cores. In general, ^{137}Cs peaks and either the CRS model and/or the CFCS model showed very good agreement, and in only two cores the CRS model had to be adjusted to achieve the best fit. The CIC model was found to deliver inconclusive dating results in six out of eleven cores, as the dates moved up and down with depth. In four cases the CIC model achieved similar results to the CFCS- or the CRS model. The dating results in this study are thus similar to what was found in previous studies which determined the CRS model to be the most reliable dating model.

Chapter 4

Salmon-derived POPs, nutrients and organic matter in surface sediments

4.1 Introduction

The importance of salmon-derived nutrients for their nursery-systems has been investigated long before the transport of contaminants became an issue. Probably the first study on nutrient deposition from salmon carcasses in Karluk Lake was published in 1932 [80]. More studies followed in the 1960's, e.g. about the sockeye salmon related phosphorus budget in Iliamna Lake [33], and the 1970's, e.g. dealing with the phosphorus contribution of sockeye spawners in Russian lakes [87]. Excellent reviews about the importance of salmon-derived nutrients to freshwater ecosystems have been published by Naiman et al. [115] and Kline et al. [84]. All studies found that Pacific salmon are major contributors of nutrients to their nursery freshwater systems, and it has been proposed that currently declining salmon stocks might lead to a further decrease in juvenile salmon survival due to a lack of fertilizing salmon-derived nutrients (e.g. [1, 135]).

Sufficient exposure to contaminants like PCBs decreases survival of juvenile chinook salmon. In contaminated urban estuaries of Puget Sound, Washington, Stein et al. [142] found that juvenile chinook salmon are subject to increased exposure to toxic chemicals during their 1–6 months residency in urban estuaries, and that this increased exposure causes the induction of a detoxifying enzyme (cytochrome P4501A). Studies by Arkoosh et al. [5, 6] showed that juvenile chinook salmon from polluted estuaries are more susceptible to disease, and thus have a lower chance of survival. Although the contamination of urban estuaries is augmented by anthropogenic point sources and likely to be much higher compared to remote environments [18], the most important route of exposure of lipophilic contaminants (e.g. PCBs, DDT) is through diet [142]. Lower concentrations of POPs in physical media of remote regions can still lead to remarkably high concentrations in top predators due to factors such as slow growth rates, high lipid concentrations, and biomagnification [45]. Currently PCB concentrations < 1 ng/l in northern waters [75, 136] support concentrations of ~2,500 ng/g lipid weight in salmon [41] and up to 146,300 ng/g lipid weight in male southern resident killer whales from the west coast of Canada, which feed mainly on salmon [130].

Biomagnification into migratory animals provides a mechanism to focus contaminants geographically. Ewald et al. [41] concluded from an Alaskan study that salmon migration provided a significant source of the contaminants cycling in a salmon nursery lake compared to a lake receiving no salmon. Salmon accumulate more than 95% of their body mass in the ocean, and after reaching maturity, return to their natal streams and lakes to spawn and die [44, 115]. The salmon stop feeding as soon as they enter freshwater, and through mobilization of fat reserves, contaminants are re-distributed to internal organs such as gonads [41]. The survival advantage to fry of delivering marine nutrients to the oligotrophic lakes [44, 84], may now be offset in part by the concurrent delivery of contaminants.

To quantify the importance of salmon as biotransporters of contaminants, sediments of nursery lakes with a wide range of salmon returns were analyzed for PCBs and selected organochlorine (OC) pesticides. This chapter presents the results of the surface sediment analyses, which have been published in two papers [89, 88].

The delivery of salmon-derived nitrogen, carbon and organic matter to nursery lakes and possible consequences for contaminant absorption will also be discussed.

4.2 Methods

This chapter includes results from the contaminant and isotope analysis of the surface sediments from the lakes listed in Table 4.1 only.

The methods for contaminant and isotope analysis used in this study are described in detail in Chapter 2, methods of calculating sedimentation rates and focusing factors can be found in Chapter 3.

Briefly, surface sediments from lakes in Alaska and northern B.C. (Table 4.1) exhibiting a wide range of salmon-return densities from 0 to 40,000 spawners were collected during 1995, 1997, 1998, 2002 and 2003. Surface sediments (0–2 cm in thickness) representing the past 5.3 ± 3.5 years of accumulation on the basis of calculated sedimentation rates, were extracted for PCB and OC pesticide analysis. PCB and OC pesticide concentrations in muscle tissue of sockeye salmon were measured to identify the signature of the salmon source. Percent carbon and nitrogen, and isotopic composition (δ^{15}N and δ^{13}C) was also determined for sediment and salmon samples. Sedimentation rates were calculated for all lakes except for Upper Olga sediments taken in 1998, and focusing factors were calculated for all lakes except Upper Olga (1998 core) and Spiridon Lake. Bulk organic matter in the sediments was measured by loss of ignition (LOI).

Table 4.1: Site location, coring years and morphometric characteristics of the lakes sampled.

Site	Location	Lat(N)	Long(W)	Coring Year	Lake Area (km^2)[a]	Lake Depth max. (m)[a]	Watershed Area (km^2)[a]
Becharof	Alaska Mainland	58°03'	156°15'	1995	1172	181	3379.45 [141]
Iliamna	Alaska Mainland	59°30'	155°	1997	2662	393	16888.15 [141]
Upper Ugashik	Alaska Mainland	57°24'	157°18'	1995	212.71	~150	1291.74 [141]
Frazer	Kodiak Island	57°16'	154°08'	1998, 2002	16.6	59	181 [90]
Karluk	Kodiak Island	57°25'	154°05'	1995, 2002	39.4	126	282 [85]
Red	Kodiak Island	57°15'	154°20'	1998, 2002	8.4	48	43.8 [69]
Spiridon	Kodiak Island	57°72'	153°68'	2002	9.2	80	> 60 [91]
Upper Olga	Kodiak Island	57°04'	154°10'	1998, 2002	7.9	70	40.1 [69]
Meziadin	B.C.	56°03'	129°16'	2003	34	133	530 [50]
Kinaskan	B.C.	57°35'	130°08'	2003	28.7	N/D[b]	1251

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[a] Information was taken from refs [50, 69, 91, 85, 90, 141].

[b] There was no depth data available for this lake.

4.3 Results and Discussion

4.3.1 PCB concentrations in surface sediments for all years combined

ΣPCBs sediment concentrations across all lakes ranged from 0.6–20.8 ng g^{-1} dry weight (Table 4.2). ΣPCB concentration is closely related to salmon spawner density as are many individual congeners (Figure 4.1). The congeners presented in Figure 4.1 include congeners particularly elevated in salmon and provide a broad overview of the ~100 congeners analyzed. For PCB 6 there seems to be a slight increase with increasing salmon spawners, but in several sediment samples collected from lakes with high spawning density PCB 6 is not detectable. Overall, the relationship between PCB concentration and salmon density is best for congeners that are abundant in salmon, such as PCB 101, and co-eluting congeners 138-163 and 153-132-105. The key factor explaining the relationships between PCB congener concentrations in sediments and spawner numbers in this study therefore is the congener abundance in salmon (the source), which will be discussed in more detail in Section 4.3.3.

PCB concentrations in the sediments vary not only between congeners and lakes but also among different years. The highest congener concentrations were found for PCBs 101, 153-132-105 and 138-163 in Red Lake sediments from 2002 (Figure 4.1; 40,000 spawners), with concentrations up to 1.7 ng g^{-1} dry weight (8.2% of the sum PCBs for this lake). The concentrations in Red Lake sediments cored in 1998 are, for the most part, less than half of those from 2002. Although this concentration discrepancy is true for some of the congeners presented in Figure 4.1, it is not consistently true for all of the remaining congeners examined. Thus, ΣPCB concentrations in Red Lake are similar for both years and reach 17.5 ng g^{-1} dry weight in 1998 and 20.8 in 2002 (Table 4.2).

Lake sediment contaminant concentrations reported in other northern climates exhibit ΣPCB concentrations similar to those found here (Table 4.2). Muir et al. [114] obtained concentrations (sum of 90 congeners) between 2.4 and 38.5 ng g^{-1} dry weight for sediments from lakes spanning the Canadian Arctic and Subarctic. Rawn et al. [123] found similar concentrations (sum of 104 PCB congeners) of 2.2–33.5 ng g^{-1} dry weight in Yukon Lake sediments. Gubala et al. [58] compared two Alaskan lakes and reported PCB concentrations (61 congeners) of 0.2 and 30.7 ng g^{-1} dry weight. Although salmon are not reported as a source of contaminants to these lakes, some of the PCB concentrations are higher when compared to the highest salmon receiving lake in this study.

However, the authors of two of the studies (see [123, 58]) mention the possibility of anthropogenic point sources, which could explain the high PCB values in the the more contaminated lakes (also see Section 4.3.4).

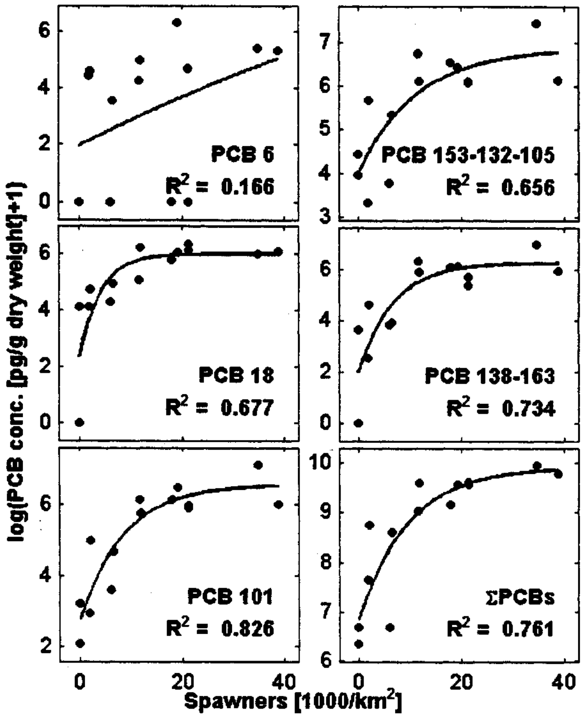

Figure 4.1: PCB concentrations of surface sediments from the years 1995–98 and 2002/03 combined, plotted against the number of spawners returning to the lakes. PCBs (pg g^{-1} dw) are log[concentration + 1] transformed. Surface sediments included 0–2 cm representing the most recent 5.3 ± 3.5 years. Therefore, the escapement data were averaged over a 10-year period, starting with the coring year. The standard deviation for salmon densities over the past ten years (starting with the coring year) was on average about 50% of the mean for each lake. PCB 6 was fitted with a straight line; for the other congeners and ΣPCBs, the equation $y = p_3 + p_2 * (1 - \exp(-x/p_1))$ was used.

Table 4.2: Escapement Numbers (i.e., number of salmon returning to the nursery lake), ΣPCB concentration and ΣPCB focus-corrected accumulation data for the lakes examined in this study, as well as comparison data from other studies.

Lakes	Escapement (Spawners km^{-2})[a]	ΣPCB concentration (ng g^{-1} dw)	ΣPCB foc.-cor. accumulation (ng m^{-2} yr^{-1})
Cored 2002/03			
Spiridon	0	0.6	N/A[b]
Kinaskan	0	0.8	125.7
Meziadin	5966	0.8	194.6
Frazer	11662	8.4	309.5
Upper Olga	17897	9.4	337.1
Karluk	19207	14.3	585.6
Red	34731	20.8	816.9
Cored 1995–98			
Becharof	1827	2.1	228.4
Iliamna	2147	6.3	287.9
Upper Ugashik	6442	5.4	426.2
Frazer	11864	14.6	579.4
Upper Olga	21274	15.1	N/A[b]
Karluk	21366	14.3	662.1
Red	38799	17.5	635.6
Other Studies			
Muir et al. [114]	N/A[c]	2.42–38.5	110–4250
Gubala et al. [58]	N/A[c]	0.2–30.7	6.3–241.2
Rawn et al. [123]	N/A[c]	2.19–33.5	1350–11500

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[a] Escapements are based on 10-year averages, starting with the coring year.

[b] There were no ^{210}Pb data available to calculate focus-corrected accumulation.

[c] There were no escapement data available.

4.3.2 PCB concentration, deposition and focus-corrected deposition in cores from 2002/03

Although the delivery of PCBs from ocean to lakes by salmon is clear and can be fairly easily estimated (escapement (kg/yr) × concentration (ng/kg)), the mechanisms and efficiencies of PCB transfer to food webs and sediments within lakes, is more difficult to quantify. Feeding on salmon eggs and on salmon carcasses in the watershed promotes direct entry of PCBs to aquatic food webs [41], but a portion of the contaminant load will be directly released into the lake, where it may partition into the organic matter of particles. The particles sink to the bottom of the lake, and through resuspension focus into depositional zones of the lake.

To examine the potential effect of sedimentation rate and focusing on PCBs in sediments, we considered only the 2002/03 cores where PCB concentrations are normally distributed and thus may be plotted without transformation. The restriction to the 2002/03 data also avoided the statistical problem of pseudoreplication.

The 2002/03 data show a linear positive relationship between PCB concentrations and numbers of spawners for all of the congeners (Figure 4.2A). PCB 6 shows a very weak relationship between concentration in sediment and escapement, which is expected because it has the lowest abundance in salmon. The remaining congeners in Figure 4.2A, however, display strong relationships between concentration and escapement. The strength of these relationships appears robust considering that no allowance has been made for diluting or concentrating effects due to varying sedimentation rates.

Deposition flux of PCBs to surface sediments, estimated from sedimentation rate, is not related as strongly as surface PCB concentration to the number of spawners (compare Figure 4.2B with 4.2A). A possible explanation for the reduced R^2 is that the total sedimentation, which includes organic and inorganic components, does not account for dilution or concentration of contaminants within the sedimenting material. For example, a lake with higher inputs of inorganic materials with low affinity for organochlorine compounds such as PCBs would exhibit a lower than expected rate of contaminant deposition. Wong et al. [151] compared contaminants in sediment cores from Lake Ontario and found that the variability in contaminant accumulation rates is greatly reduced when sedimentation rates are corrected for focusing. Focus correction for our data, applied by dividing PCB deposition by the focusing factor, results in noticeable improvement of the relationship between PCB deposition and escapement for ΣPCBs and most of the congeners, with the exception of PCB 6 (Figure 4.2C). The improvement in the relationship evident between focus-normalized PCB deposition and escapement implies that PCB inputs from salmon are thoroughly mixed and distributed within each lake. A localized input of salmon-derived PCBs could lead to a much higher loading of contaminants in a core taken close to the source, or a lower loading when the core is taken far away from the localized input. In cases where PCB variability is produced by processes other than sediment redistribution, focus correction would not improve the relationship [151].

Similarly to what was found for the PCB concentration, the PCB fluxes observed in lakes from this study are often lower compared to some of the lakes in the other studies (Table 4.2, also refer to Section 4.3.1). Rawn et al. [123] reported values of ΣPCBs between 1,350 and 11,500 ng m^{-2} yr^{-1} for lakes in the Yukon. Gubala et al. [58] calculated fluxes of 6.3 and 241 ng m^{-2} yr^{-1} for their lakes in Alaska. This study is probably the best comparison to ΣPCB fluxes of our non-salmon lakes, which are in the range of 130 ng m^{-2} yr^{-1}. The ΣPCB fluxes observed by Muir et al. [114] span 110–4,250 ng m^{-2} yr^{-1} for midlatitude, sub-Arctic and Arctic lakes.

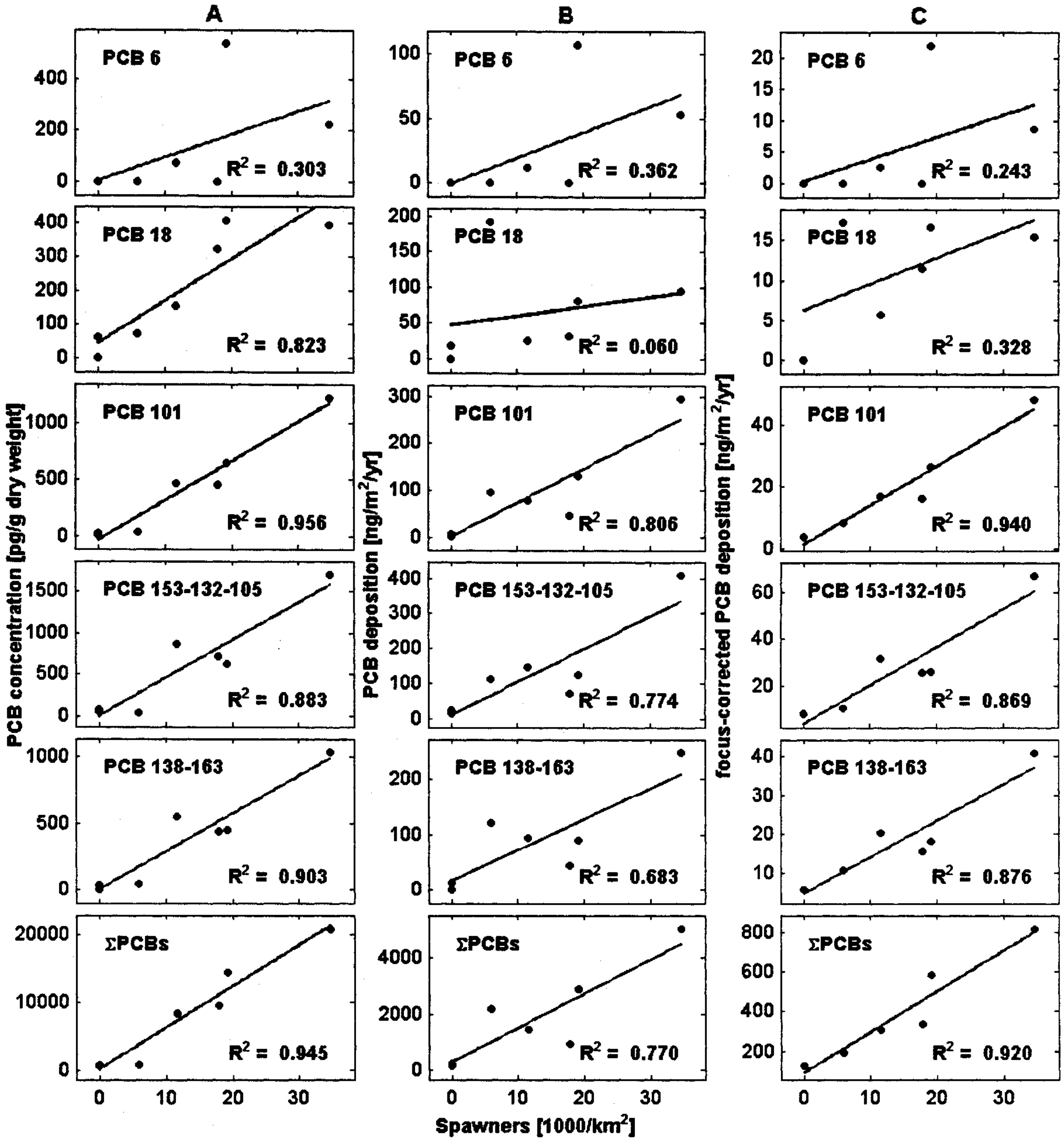

Figure 4.2: Surface sediment PCB loadings for the years 2002/03. Plotted are (A) PCB concentrations, (B) PCB deposition, and (C) focus-corrected PCB deposition against density of spawners. The PCB data are not transformed, and all plots are fitted with a straight line.

4.3.3 The importance of PCB congener abundance in salmon

As indicated earlier, the factor influencing the relationship between contaminant loading of the sediments and number of spawners will be mostly determined by the abundance of a particular congener in salmon. Figure 4.3 illustrates this with a comparison between the patterns and concentrations of PCBs in the surface sediments of Frazer Lake (which has annual salmon returns of 11,700 fish per km^2) to those of spawning sockeye returning to that lake (Figure 4.3a and 4.3b). In particular, the PCB congeners designated as 101, 118, 153 and 138 + 163 were among the most abundant in both sockeye salmon and Frazer Lake sediments. More telling are the concentrations and patterns in Spiridon Lake, which receives no salmon spawners (Figure 4.3c). Concentrations of PCBs in sediments from this lake are tenfold lower, and include a greater proportion of lighter congeners, which are more effectively transported by air than the more chlorinated congeners [114].

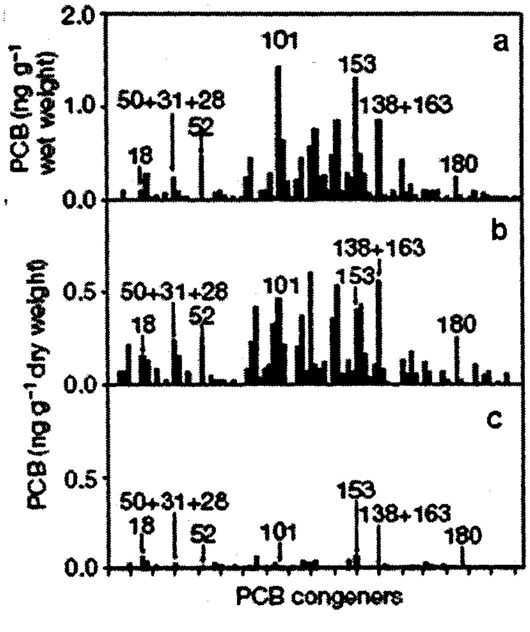

Figure 4.3: Comparisons between pattern of PCB congeners between surface sediments in Alaskan lakes and sockeye salmon muscle tissue. **a-c**, PCB congener patterns (numbers represent different congeners) in **a**, sockeye salmon from Frazer Lake; **b**, surface sediments from Frazer Lake (total escapement of ~ 11,700 spawners per km^2); and **c**, surface sediments from Spiridon Lake (no anadromous salmon return).

Generally, studies looking at PCBs in fish often find elevated concentrations of congeners such as PCB 153, 101, 138 and 180 [118, 54]. Since most of these congeners also show a tight relationship of sediment PCB load to spawner numbers in this study, relative abundances for PCB congeners in the sockeye salmon from all 2002/03 lakes were calculated. The data include 5 sockeye salmon each from Frazer, Upper Olga, Karluk and Red Lake, and 3 sockeye salmon from Meziadin Lake. We indeed found highest abundances for PCB 153-132-105 (10.2%), followed by PCB 101 (9.8%) and PCB 138-163 (5.6%), whereas relative abundances for the other congeners shown were 1.5% for PCB 18 and 0.6% for PCB 6.

The plotted congeners therefore suggest that the strength of the relationship between contaminant loading in the sediments and numbers of spawners is greatly influenced by the relative quantity of each particular congener transported in the salmon. All plots show consistently good fits for PCBs 101, 153-132-105, and 138-163. It is not surprising that the relationship for 153-132-105 is somewhat less strong than that for PCB 101, because the method did not discriminate congeners 132 and 105 from PCB 153. Only congener 153 is particularly known to accumulate in fish, and varying proportional loadings of congeners 132-105 will reduce the relationship.

Another indicator for the strength of a linear relationship $y = ax + b$ between two variables is the slope, a, whereby a steeper slope indicates a higher significance of the dependence of y on x [140]. Since the relationship between PCB loading in the sediments and escapement appears to depend on the relative abundance of the particular PCB congeners in the transporting salmon, more abundant congeners in salmon should show higher values of a in the regression equations. We therefore calculated slopes of the obtained regressions between PCB concentration and escapement for all of the congeners, and plotted them against the relative abundance of the congeners in salmon (Figure 4.4). Only slopes from regressions with an $R^2 > 0.2$ were included, and the data were log transformed. As expected, an increase of slope values is observed for congeners that are more abundant in sockeye salmon. It is important to note that this relationship was found only for sockeye salmon and sediment data from the same year. Slopes derived for surface sediments from 1995–98 yielded no relationship with salmon data from 2002/03.

It was mentioned earlier that PCB concentrations in the sediments varied between the different years for some congeners, but that similar ΣPCB concentrations have been delivered. A principal components analysis (PCA) performed on surface sediment PCB data from all lakes together with PCB data from all salmon samples, further highlights the differences in PCB congener patterns for the sediment samples of different years (Figures 4.5 and 4.6). Before the PCA was conducted, the PCB data were screened such

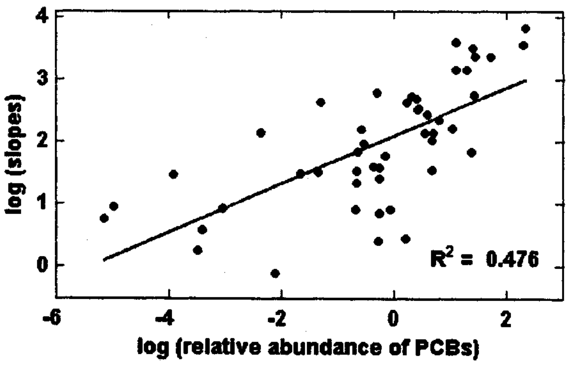

Figure 4.4: Slopes of the relationship of the PCB concentration in surface sediments from 2002/03 versus salmon spawners are plotted against the relative abundance of PCBs in sockeye salmon from 2002/03. The data are log-transformed and fitted with a straight line.

that only those congeners were included that were present in > 50% of all samples, and > 5% in at least one sample. A PCA of the remaining 16 analytes revealed that 76% of the variance can be explained by the first three principal components. A score plot of the first two principal components shows separations between the surface sediments of the salmon lakes cored in 1995/98 and Meziadin Lake, the salmon lakes cored in 2002, and the salmon samples on the first axis (PCA1) (Figure 4.5). PCA1, which alone explains 47% of the variance, reflects the dominance of PCB congeners 101, 153-132-105, 138-163 and 183, which are the most abundant congeners in the salmon samples and have the highest positive loadings on PCA1 (see Figure C.1 in the Appendix). Interestingly, all the salmon samples cluster together, and show no grouping according to nursery lake, spawning region (Alaska vs B.C.), or year (2002 vs 2003 vs 2004). Some salmon samples group closer to the 2002 surface sediments, causing almost a smooth transition between the 2002 surface sediment samples and the salmon samples, and thus further emphasizing the similarity of PCB congener patterns between the two. Along the second axis (17% of the variance explained) there is a separation between surface sediments of Kinaskan (non-salmon receiving lake in northern B.C., cored in 2003), the surface sediments of the salmon lakes and Spiridon Lake (non-salmon receiving lake in Alaska, cored in 2002). PCA2 is distinguished by high positive loadings of PCB 147-107, as well as 44 and 50-31-28, and negative loadings of lower chlorinated PCBs 18 and 15-17 (Figure C.1). The third principal component, which explaines another 12% of the variance, separates Spiridon from all the other samples (Figure 4.6), and is associated with high positive loadings of

PCB 18, 153-132-105, and 87-81 (Figure C.1).

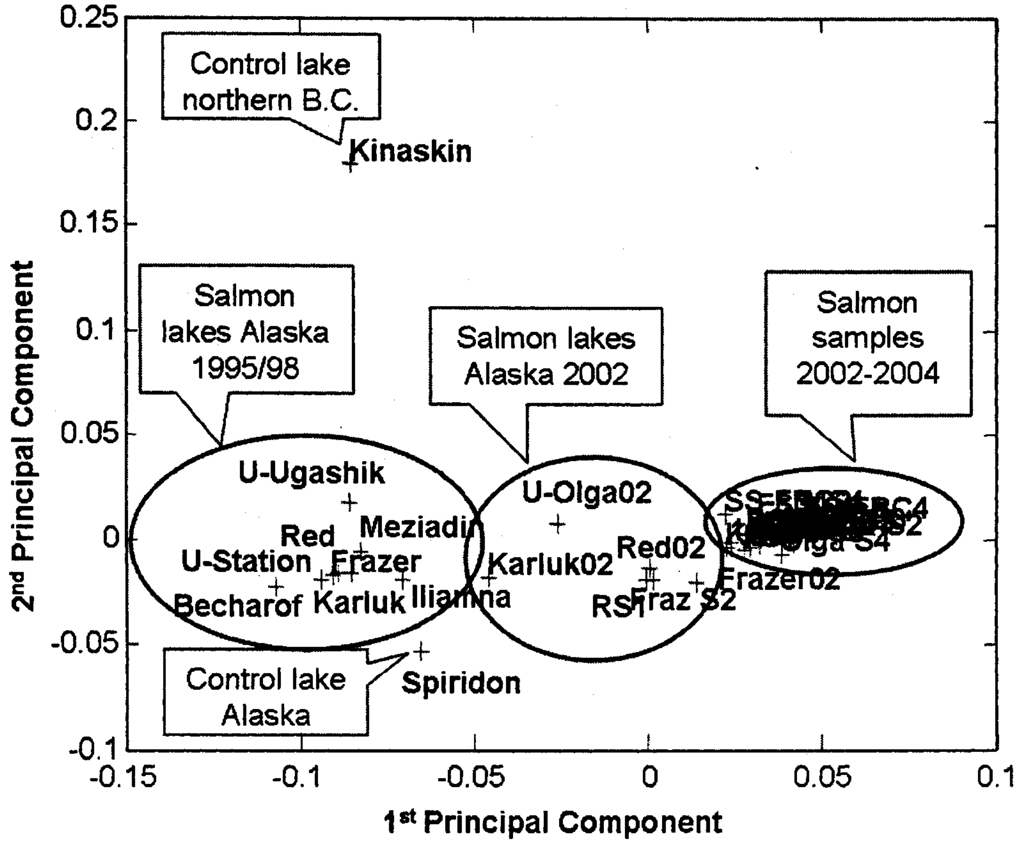

Figure 4.5: Score plot of the first two principal components. The PCA included all surface sediment samples, as well as all salmon samples (n = 41). The PCB congener data were screened to only include analytes that were present in > 50% of all samples, and > 5% in at least one sample. 16 analytes remained.

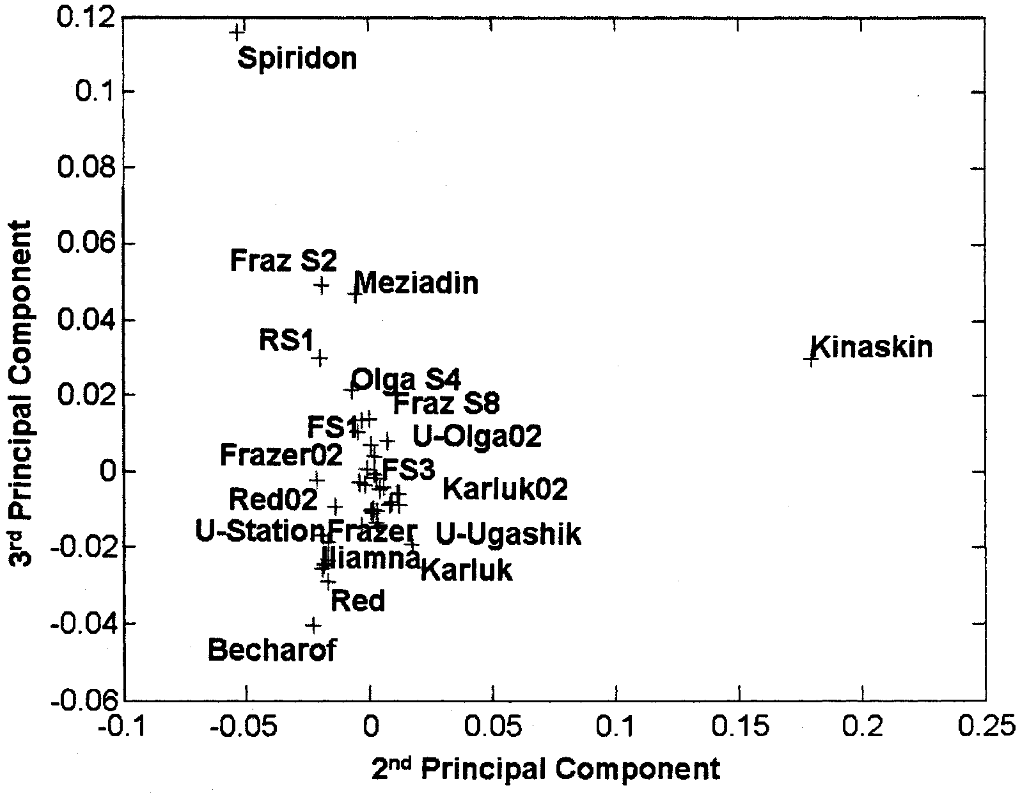

Figure 4.6: Score plot of principal component 2 and 3.

The fact that the two control lakes do not group together might reflect differences in atmospheric PCB deposition in regions, or years. Since Spiridon is situated relatively close to the Alaskan salmon lakes (geographically as well as in Figure 4.5), it is conceivable that this lake is influenced somewhat by atmospheric transfer of off-gassing PCBs originating from decaying salmon carcasses.

One explanation for a shift in congener patterns in sediments from 1995–98 versus sediments from 2002/03 could be that congener patterns in salmon vary at a scale similar to salmon oceanic lifetimes (~3 years). Such a shift in PCB patterns would require a similar shift in the food foraged by salmon at sea which itself would depend on spatial or temporal variation in PCB patterns in the upper ocean. The SHEBA project collected PCB data that clearly show PCB pattern shifts between Arctic interior water-masses and water-masses originating in the Pacific Ocean or on the Arctic's shelves [98]. Fish data might provide further insight into variations in fish foraging patterns and PCB fingerprints. Unfortunately there are no historical data of PCB concentrations in Alaskan salmon available, which would enable us to test whether temporal trends in salmon PCB loadings exist, and whether those trends can be recovered in sediments of salmon receiving lakes. However, changes of PCB congener patterns with depth in sediments have been reported previously [151, 39, 117] and could plausibly be attributed to a shift in PCB input patterns. Hence, there is circumstantial evidence that PCB congener patterns vary in the ocean leading to changes in the PCB pattern carried by salmon spawners, and that these changes will be reflected in variation of congener patterns in the sediments. Further analysis will be needed to test this hypothesis.

4.3.4 Organochlorine (OC) pesticides in surface sediments from 2002/03

The analysis of the OC pesticides was often difficult, and not all analytes could be reliably identified. Especially in the samples from 1995–98 important analytes such as the DDTs could not be identified due to interference with other compounds. For that reason, OC pesticides results will be restricted to the surface sediments from 2002/03. The compounds that could be detected in most of the surface sediments from 2002/03 ($n = 7$) are presented in Table 4.3, with the number of non-detects indicated in the last column. As in the case of the PCBs, several OC pesticides were found to be significantly related to salmon spawner densities. The pesticides that showed significant relationships at a level of at least $p \leq 0.1$ included 3 of the 4 DDT analytes, the two chlordanes, as well as γ-HCH (Table 4.3). With the exception of γ-HCH, all these compounds had a relative abundance in salmon of $> 3\%$, and a log K_{OW} of ≥ 6.0, but not exceeding 7. Both of these parameters can be expected to play an important role for the relationship of contaminant concentration in the sediments and spawner densities. A contaminant with a higher log K_{OW} (in the range of 5.9–7.5, see [26]) is more likely to biomagnify in the foodchain, as well as to sorb to organic matter and accumulate in the sediments (e.g., [21, 55, 27, 117]). The importance of the abundance of a contaminant in salmon was already discussed above, although the significance of the relationship here seems to be not directly influenced by the magnitude of the relative abundance of the pesticide in salmon alone. For the DDTs for example, p,p'-DDT shows the best relationship, although it has a lower relative abundance in salmon compared to p,p'-DDE. It is possible that due to interferences of some PCBs with some DDTs (e.g., PCB 85 sometimes interferes with p,p'-DDE, and PCBs 114-134-131 with o,p'-DDT and p,p'-DDD), the contaminant analysis for the pesticides was not precise enough to pick up such differences. The fact that DDT is metabolized to DDE and DDD in salmon and sediments respectively, will very likely cause changes in the relationships, as well.

Methoxychlor, which has a relative abundance of 5.7% in the salmon, was rarely detected in the sediments, the same is true for Dieldrin, which has a relative abundance in salmon of 2.6%. The relationship of α-Endosulfan, which appears to be significant in Table 4.3, is based on only three values. HCB, which had a relative high abundance in salmon and also has a log K_{OW} of 5.5, would show a significant relationship if Kinaskan Lake would be excluded. The HCB value in Kinaskan was high compared to the other lakes, and although the reason is not apparent, it seems to be a true value and was thus kept. Interestingly, γ-HCH is significantly related to number of salmon spawners, although it was not very abundant in salmon samples and also has a relatively low log K_{OW}. Usually it is expected that compounds such as γ-HCH are effectively transported by air and water [17]. It was shown by Jeremiason et al. [78], that more productive lakes have enhanced net gas absorption of chemicals, as well as lowered net volatilization fluxes. Since higher sockeye spawner returns also increase the productivity of the nursery lakes (see below), it is possible that the relationship of γ-HCH with salmon spawners is due to enhanced absorption and/or lower volatilization fluxes, and thus a secondary effect of spawner abundance in the nursery lakes.

The influence of corrections for sedimentation rate and focus corrected fluxes on the relationship between OC pesticide concentration in the surface sediments and number of sockeye salmon spawners was similar to what was found for the PCBs. The relationships got worse when just corrected for sedimentation rate, and were better again after corrected for focusing (data not shown). Because no ^{210}Pb data were available for Spiridon Lake, and a focus correction was therefore not possible for this lake, relationships for focusing corrected fluxes are based on 6 lakes only. Since several compounds were also not detected in all samples, it was decided that the data points were too few to allow for a meaningful comparison of significances of pesticide concentration and corrected flux relationships with the number of salmon spawners.

Table 4.3: Linear regressions of the organochlorine pesticides in the surface sediments from 2002/03 against salmon escapement.

Compound	% Abundance in salmon	Log K_{OW}	R^2	F-statistic probability	Number of non-detects
α-Chlordane	10.2	6.0, 5.5	0.523	0.066	1
γ-Chlordane	3.1	6.0, 5.5	0.784	0.08	none
α-Endosulfan	0.8	3.83, 4.1	0.607	0.039	4
β-Endosulfan	2.1	3.5, 4.1	$4.7*10^{-7}$	0.999	3
α-HCH	0.7	3.8	0.034	0.695	5
γ-HCH	0.3	3.8	0.597	0.0417	1
Aldrin	0.2	3.01	0.197	0.318	4
Dieldrin	2.6	5.2, 5.37	0.013	0.811	4
Endrin	0.1	5.2, 5.06	0.206	0.306	6
HCB	9.5	5.5	0.0002	0.975	none[a]
Heptachlor	0.1	4.4–5.5, 6.1	0.271[b]	0.231	3
Heptachlor Epoxide	0.1	3.65, 5.4	0.426[b]	0.112	3
Methoxychlor	5.7	4.68–5.08	0.061	0.594	4
PECB	0.5	4.8–5.18	0.129	0.428	1
o,p'-DDT	14.6	6.19, 6.53	0.458	0.094	1
p,p'-DDD	7.5	6.19	0.106	0.475	1
p,p'-DDE	32.1	6.19	0.591	0.043	1
p,p'-DDT	10.1	6.19	0.781	0.008	none
ΣDDT	64.3	6.19	0.75	0.011	none

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[a] Kinaskan outlier

[b] negative relationship

Comparisons of concentrations and focus corrected fluxes of selected OC pesticides in this study with other studies conducted in northern regions are presented in Table 4.4. Fluxes were calculated by multiplying contaminant concentration by the sedimentation rate, and dividing by the focusing factor. In general, concentrations and fluxes found in this study are within the range of the other studies presented in Table 4.4. The values in the study by Rawn et al. [123] are usually higher, with fluxes up to 13,000 ng m^{-2} yr^{-1} for ΣDDT. Some of the differences are due to more compounds that were included in the sums recorded, but the authors also investigated lakes in the Yukon, some of which had direct input of contaminants (e.g. application of DDT, HCH and HCB for insect control, as well as application of waste oil to retain ice-free strips of water). The fluxes in Rawn et al.[123] (Table 4.4) are much higher compared to the concentrations, because the authors averaged fluxes between 1985 and 1995, which included sub-surface maxima in some cases. The best comparison to our data, especially for lakes receiving no salmon, is probably the study of two lakes in Arctic Alaska by Gubala et al. [58]. Their values are in the low range, with OC pesticide concentrations well below 1 ng g^{-1} dry weight, and fluxes not exceeding 7.1 ng m^{-2} yr^{-1} (Table 4.4). Values like this would be expected for remote lakes in that location which receive contaminants through atmospheric input only. The study by Muir et al. [113] also looked at lakes in remote locations with atmospheric input, but they spanned a wide latitude range reaching from 49°N to 81°N. Their highest value of 9.96 ng g^{-1} dry weight for ΣDDT was found in a more southerly lake (49°N), whereas other lakes in higher latitudes showed values closer to those found in our study (e.g. 1.54 and 5.11 ng g^{-1} dry weight for latitudes of 63°N.). It should also be noted that values presented here reflect more recent deposition compared to the data of Gubala et al.[58] and Muir et al.[113], which were collected in the mid-1990's.

Table 4.4: Concentrations and focus corrected fluxes of selected organochlorine pesticides in this study, and comparisons with other studies conducted in northern regions.

Reference	ΣDDT[a]	ΣHCH[b]	ΣCHL[c]	HCB[d]
Concentration (ng g^{-1} dry weight)				
This study	0.1–5.42	0.02–0.5	0.03–2.73	0.05–0.63
Rawn et al.[123]	0.08–3.47	0.13–1.37	0.04–3.87	0.06–1.14
Gubala et al.[58]	0.05, 0.57	0.19, 0.81	0.04, 0.4	N/D[e]
Muir et al.[113]	0.11–9.96	0.05–0.9	< 0.01–1.9	0.09–1.8
Focusing corrected accumulation (ng m^{-2} yr^{-1})				
This study	3.6–212.11	3.68–77.03	7.64–107.29	1.70–99.08
Rawn et al.[123]	66–13,000	75–357	33–649	42–870
Gubala et al.[58]	1.9, 4.5	6.4, 7.1	1.3, 3.1	N/D[e]
Muir et al.[113]	5.0–690	30–54	3.4–42	32–81

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[a] Sum of p,p'-DDE, p,p'-DDD, o,p'-DDT and p,p'-DDT for this study and Muir et al., Rawn et al. also included o,p'-DDD and o,p'-DDE. Gubala et al. did not specify.

[b] Sum of α-HCH and γ-HCH for this study and Muir et al., Rawn et al. also included β-HCH. Gubala et al. did not specify.

[c] Sum of cis- and trans-Chlordane for this study and Muir et al., Rawn et al. also included heptachlor, trans-nonachlor, cis-nonachlor, and heptachlor epoxide. Gubala et al. did not specify.

[d] Sum of 1,2,3,4-tetrachlorobenzene, pentachlorobenzene and HCB in Rawn et al.

[e] Value was not determined.

4.3.5 Salmon-derived nutrients and organic matter in surface sediments

To determine whether sockeye spawners transport nutrients to sediments on spatial scales similar to the contaminants in this study, we plotted percent carbon, nitrogen, organic matter (in form of LOI = loss of ignition) and C/N against spawner abundance for all lakes (Figure 4.7A-F). Significances of the relationships can be found in Table 4.5. To avoid the statistical problem of pseudoreplication, the two groups representing different years (95–98 and 02/03) were treated separately when looking at the significance of the relationship. Table 4.5 shows that all relationships were significant at a level of $p < 0.05$, except the acid treated C/N, and the untreated %C in the 1995–1998 surface sediments. The %C was determined with GC-MS (see Chapter 2 - Methods), and to ensure that only organic carbon is detected, the sediments have to be acid treated to remove inorganic carbon. This was not possible for the 2002/03 sediments because we did not have enough sediments left for acid treatment. Apparently, the inorganic carbon fraction in those sediments was either not very different for the various lakes, differed in a similar way as the organic carbon fraction, or was only a small portion of the total carbon in these lakes, since the relationship was significant (Figure 4.7C and Table 4.5). For the 1995–98 sediments, the relationship was significant only after inorganic carbon was removed (Figure 4.7D and Table 4.5).

It should be noted that the significant relationship of %C with escapement is most likely not due to carbon directly transported by the salmon, but rather a secondary effect of enhanced lake productivity caused by high numbers of salmon spawners. This is supported by the negative relationships of C/N values with escapement in the surface sediments from 1995–98 (not acid treated C) and 2002/03 (Figure 4.7E and Table 4.5). These relationships show that with higher spawner numbers, the proportion of nitrogen rises more significantly compared to that of the combined (organic and inorganic) carbon. For the acid treated sediments of 1995–95, the relationship between C/N and escapement does not display a clear trend, and appears to be relative consistent throughout the spawner gradient (Figure 4.7F). Nevertheless, the poor relationship of δ^{13}C with escapement (Figure 4.8, also see text below) suggests that the %C recorded in the sediments does not originate directly from salmon, but is due to the enhancing effect of salmon-derived nutrients on lake productivity.

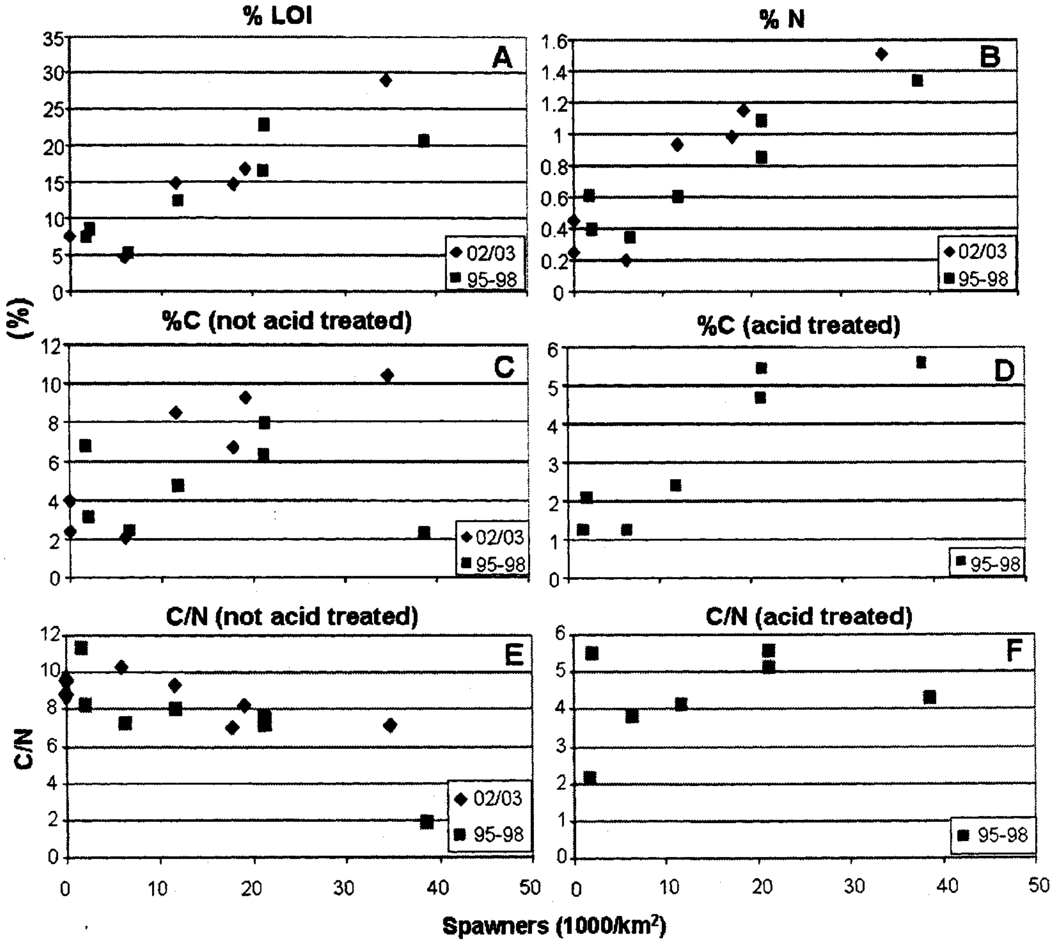

Figure 4.7: Percent loss of ignition (LOI = organic matter) (A), percent nitrogen (B), percent carbon (C, not acid treated; D, acid treated), and C/N (E, not acid treated; F, acid treated) in surface sediments plotted against escapement.

The positive impact of salmon spawners on lake productivity is further indicated by the increase of organic matter with higher escapement (Figure 4.7A). It is likely that the organic matter is of autochthonous origin because of the low C/N values (between 2 and 6 in the acid treated sediments, see Figure 4.7F), which suggest a nonvascular aquatic plant source [107].

The relationship of %N with escapement (Figure 4.7B) on the other hand is likely a direct result of sockeye salmon spawner deposition, which is indicated by the positive relationship of δ^{15}N with number of spawners, and will be discussed in more detail below.

When looking at the limnology and fish recruitments of the lakes, salmon-derived nitrogen and phosphorus for the nursery lakes are especially crucial, since salmon spawning lakes are mostly oligotrophic, and are either nitrogen or phosphorus limited. How much nutrient is deposited by salmon spawners into their nursery systems is a subject of discussion in the literature. In this study, sediments in the highest salmon receiving lake had about 3–4 times higher values of %C and %N compared to the control lakes.

Table 4.5: Statistical significance of the relationships of percent nitrogen, percent carbon, percent LOI (loss on ignition = organic matter) and C/N with escapement for the surface sediments.

Nutrients	R^2	F-statistic probability
surface sediments 2002/03		
%C	0.74	0.013
%N	0.868	0.002
%LOI	0.838	0.004
C/N	0.635	0.032[a]
surface sediments 1995-98		
%C	0.007	0.856
%N	0.857	0.003
%LOI	0.736	0.013
C/N	0.74	0.013[a]
%C (acid treated)	0.8127	0.005
C/N (acid treated C)	0.10	0.484

---

[a] Negative relationship.

From a contaminant perspective the enrichment of organic matter to which the pollutants can be sorbed is very important. The mechanisms can be direct deposition of organic matter by decaying salmon carcasses, or higher lake productivity supported by salmon-derived nutrients, which in turn causes higher fractions of organic matter in the sediments. There are two direct consequences which can be derived from this:

1. Contaminant concentrations can not be corrected for organic matter or -carbon, as is often done in sediment studies since POPs tend to sorb to the organic fraction in the sediments. Because salmon transport both contaminants and organic matter/carbon, they are confounding factors, and correcting for organic matter/carbon would basically remove the salmon from the equation.

2. As already mentioned in Section 4.3.4, contaminants that transport by air are more likely to be absorbed in lakes that are more productive. Therefore, two mechanisms might cause higher contaminant concentrations in salmon-receiving lakes:

   A) The direct transport of contaminants by salmon into the lakes.

   B) An indirect mechanism of increased net-absorption of contaminants caused by enhanced lake productivity due to salmon-derived nutrients.

   Evidence of a process like this is given by the relationship of γ-HCH with escapement in the 2002/03 surface sediments, as shown earlier.

Stable isotope composition is frequently employed to trace the flow of nutrients in ecosystems. Especially the ^{15}N enrichment in Pacific salmon compared to other N sources in nursery freshwater systems is used to determine marine nutrient inputs [105]. Salmon-derived nutrients were found in biota and sediments of salmon-receiving freshwater systems [105, 83, 82], and in soil, wood, foliar and insect tissues of their riparian habitats [124, 103, 68]. Several studies compared δ^{15}N values directly to spawner densities, and found that δ^{15}N can be used in some lakes to track past escapement [56, 43, 44]. However, according to some studies δ^{15}N in the sediments is not linearly related to salmon escapements, and a specific two-source mixing model has to be used to estimate past sockeye spawner numbers from the δ^{15}N signature in the sediments [115, 134]. Naiman et al. [115] fitted such a two-source mixing model to sediment δ^{15}N values from 12 Alaskan lakes along an escapement gradient, which yields an asymptotic response of the δ^{15}N to numbers of spawners.

When the stable isotopes δ^{15}N and δ^{13}C were plotted against escapement for the surface sediments in this study, linear relationships of δ^{15}N with spawner densities were found in the surface sediments from both 1995–98 and 2002/03, which were significant at $R^2 > 0.4$ and $p < 0.1$. The two-source mixing model could not be employed here because such a model does not allow for denitrification in the sediments, a process that might occur in Red Lake in our study (see chapter 5). The relationship between $\delta^{13}C$ and escapement was not significant in either of the two groups, 1995–98 or 2002/03. As mentioned above, the proportion of carbon delivered by the salmon spawners is apparently negligible compared to that of nitrogen, and the $\delta^{13}C$ signal in the sediments is therefore not strong enough to achieve a significant relationship with escapement.

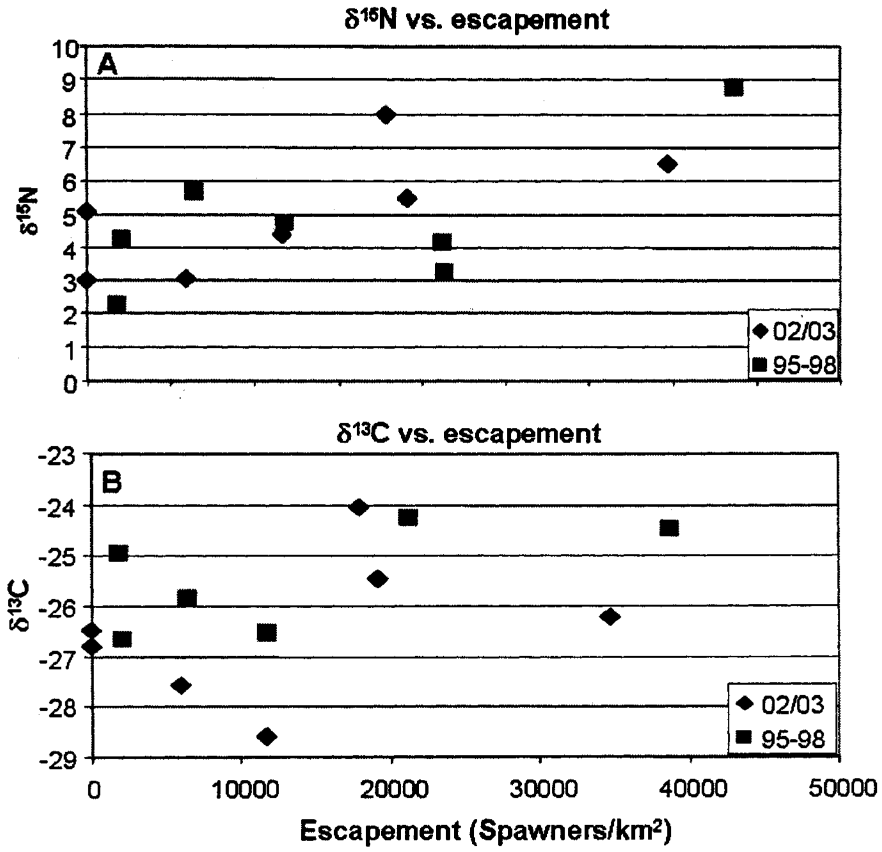

Figure 4.8: $\delta^{15}N$ (A) and $\delta^{13}C$ (B) in surface sediments plotted against escapement.

4.3.6 Conclusions

This study is the first to determine a direct relationship between the density of sockeye salmon spawners and contaminant concentrations in lake sediments. Especially for the

PCBs, linear relationships were better for congeners that had a higher abundance in salmon, and consequently, PCB patterns in the sediments of the nursery lakes resembled closely those in the salmon. Several OC pesticides with a high abundance in salmon also displayed a significant relationship of concentration in surface sediments with escapement, especially ΣDDT, which had over 60% of the relative abundance in salmon. Thus, we could show quantitatively and qualitatively that sockeye salmon are an important transport mechanism of contaminants to their nursery lakes.

Percent nitrogen, carbon and organic matter in sediments were also significantly related to escapement, which confirmed that sockeye salmon are important transporters of nutrients to their freshwater nursery systems. The often used indicator of salmon-derived nitrogen, $\delta^{15}N$, displayed a less strong relationship with sockeye salmon spawners, but was still significant at a 90% level.

One of the implications of higher lake productivity might be an increased net-absorption of contaminants transported via the atmosphere as proposed by Jeremiason et al. [78], which is a probable reason for the relationship of γ-HCH with escapement in this study. Further studies would be needed to investigate the productivity-dependent absorption of contaminants transported by the atmosphere.

Chapter 5

The use of down-core profiles to track historical deliveries of POPs by sockeye salmon

5.1 Introduction

The results in the previous chapter showed that in recent years, sockeye salmon spawners have been important transporters of POPs into their nursery lakes in B.C. and Alaska. It is likely that this mechanism has also been operating in the past, although historical tissue samples that would permit a direct comparison, are lacking. It is therefore presently not known whether salmon spawners delivered significant amounts of contaminants to their lakes in previous years, or if contaminant deliveries by other pathways, such as the atmosphere, have been prevalent. Similarly lacking are longterm historical measurements of atmospheric and oceanic contaminant concentrations, which would not only allow for the determination of global trends, but would also aid in a better understanding of the complex interactions of different contaminant pathways and impacts of changes [101]. Whenever possible, sediment cores have been used to fill this gap, e.g. by tracing natural and anthropogenic sources of contaminants, and especially to evaluate atmospheric transport of those POPs to pristine regions (e.g. [113, 114, 100, 34, 123]). Sediment cores have also been used to reconstruct historical sockeye salmon population dynamics by the means of salmon-derived nutrients and proxy indicators (e.g., δ^{15}N, diatoms), which indicates that salmon leave measurable 'fingerprints' in sediments and can be retrieved in down-core profiles [134, 56, 44, 43]. It is therefore likely that salmon-derived contaminants can be traced in down-core profiles and can be linked to past sockeye salmon spawner abundance qualitatively and quantitatively.

The objective of this part of the study was therefore to investigate whether the relationship between sockeye salmon spawners and contaminants in lake sediments can also be found historically. This was done by analyzing deeper slices of a sediment core for contaminants and other proxies, and comparing the dated data to historical counts of sockeye salmon spawners. If salmon were a dominant source of contaminant to nursery lakes in the past, we would expect higher contaminant fluxes during periods of higher salmon returns in dated sediment cores.

5.2 Methods

The methods for contaminant, elemental- and isotope analysis, as well as methods for loss of ignition are described in detail in Chapter 2, methods regarding the dating can be found in Chapter 3.

In brief, sediment cores were collected from lakes in Alaska and British Columbia. Sediments were extruded on site at fine intervals, placed in WhirlPak® bags and frozen immediately. In the lab, sediment subsamples were freeze-dried for dating, elemental- and isotope analysis, and loss on ignition measurements. Wet sediments were processed for the extraction of PCBs and OC pesticides.

For the down-core profiles, cores were included from lakes sampled in the years 2001, 2002 and 2003 (see Table 5.1). From those lakes, Kinaskan is the only one which did not receive any salmon spawners and will therefore be used to assess contaminant input from the atmosphere.

Freeze dried sediments from two lakes, Frazer and Karluk, were analyzed for total mercury (Hg). The cores were taken in 1998 and used in a previous study to reconstruct past sockeye salmon abundance using sediments records of δ^{15}N and biological indicators; dating models for these cores are described in [44].

Hg measurements were conducted using a SP-3D mercury analyzer (Nippon Instruments Corp). In the automated analyzer, freeze dried sediment samples are heated to a maximum temperature of 950°C. The released Hg is subsequently collected and isolated in a two-stage gold amalgam process. Total Hg is then measured using cold vapor atomic absorption spectroscopy (CVAAS). The analysis is sensitive to Hg concentrations as low as 0.01 ng.

Table 5.1: Site location, coring years and morphometric characteristics of the lakes for the cores included in the down-core profiles.

Site	Location	Lat(N)	Long(W)	Coring Year	Lake Area (km^2)[a]	Lake Depth max. (m)[a]	Watershed Area (km^2)[a]
Frazer	Kodiak Island	57°16'	154°08'	2002, 1998	16.6	59	181
Karluk	Kodiak Island	57°25'	154°05'	2002, 1995	39.4	126	282
Red	Kodiak Island	57°15'	154°20'	2002	8.4	48	43.8
Upper Olga	Kodiak Island	57°04'	154°10'	2002	7.9	70	40.1
Fraser	B.C.	54°05'	124°45'	2001	54	30.5	6268
Bowron	B.C.	53°13'	121°22'	2002	10.2	63.4	3403
Shuswap	B.C.	51°00'	119°00'	2002	330	162	16221
Quesnel	B.C.	52°30'	121°00'	2002	270	530	5930
Meziadin	B.C.	56°03'	129°16'	2003	34	133	530
Kinaskan	B.C.	57°35'	130°08'	2003	28.7	N/D[b]	1251

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[a] Information was taken from refs [50, 69, 91, 85, 90, 141]

[b] There was no depth data available for this lake.

Escapement data (number of sockeye salmon which return to their nursery lakes to spawn) was provided by authorities from the Department of Fisheries and Oceans (DFO) in British Columbia and the Alaska Department of Fish and Game. The data can be derived in several different ways:

1. mark and recapture;
2. counting of post-spawning mortalities;
3. counting of migrating salmon which pass a fishway or weir;
4. estimates by sonar;
5. estimates by aerial counts.

Unfortunately, there are no error estimates available for escapement data.

Usually, sockeye salmon returns exhibit a 4-year cycle, caused by their life history as explained in Chapter 1. In spawner numbers, often a 'dominant year' with very high abundance can be observed, followed by intermediate abundance ('subdominant year'), and two years with very low abundance ('nondominant years') [72]. Very pronounced spawning abundance cycles can be extremely difficult to interpret, especially when underlying trends have to be compared to patterns in sedimentary down-core profiles, where the information from many years might be stored in only a few millimeters of sediment depth. To extract trends from escapement data it is usually sufficient to fit a 4-year running average to smooth the data, and this was done for most lakes, as shown in Figure 5.1 with the example of Meziadin Lake.

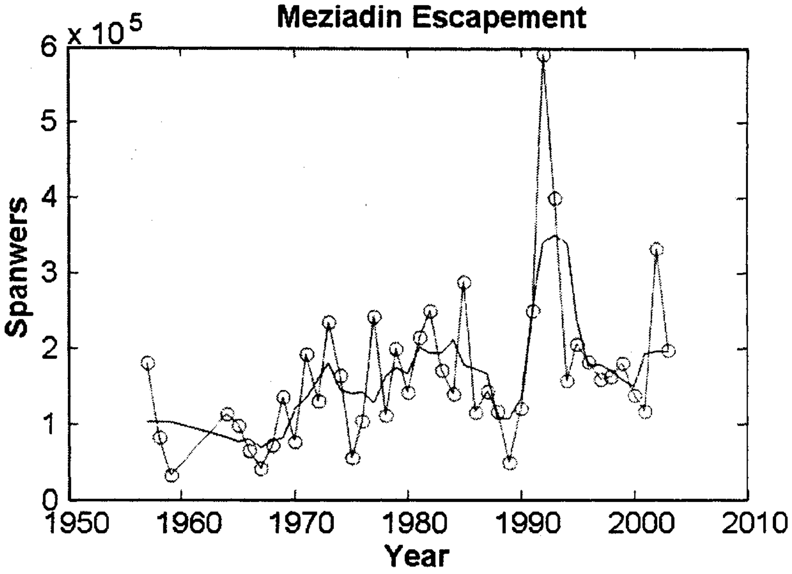

Figure 5.1: Sockeye salmon escapement numbers for Meziadin Lake as provided by DFO (open circles), and the smoothed function (4-year running average, solid line).

However, in the case of Shuswap Lake, a second, 12 to 13-year climate cycle emerged after the 4-year cycle was removed (Figure 5.2). In order to extract the underlying trend from this additional cycle, the data was fitted with a sloped cosine function $(p_1+p_5*(x-p_3)+p_2 * cos(2*\pi*(x-p_3)/p_4)$, and the residuals were then again smoothed (see Figure

5.2). The resulting curve was used to visualize the general trend of sockeye salmon abundance and to compare its pattern to that of the down-core profiles of Shuswap Lake (see below).

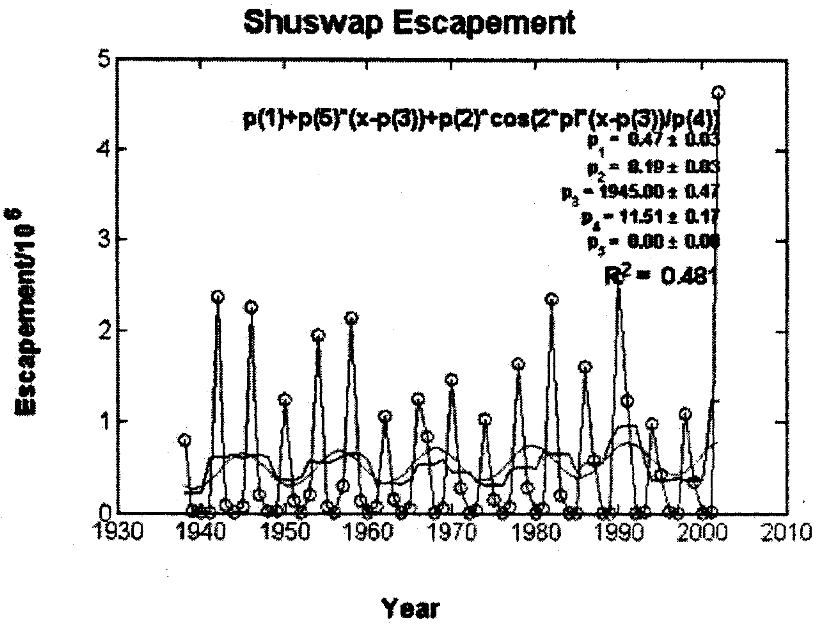

Figure 5.2: Because the Shuswap escapement-data has two overlying cycles (4-year life history cycle and a ~12 year climate cycle), first, a four-year running average was taken to remove the 4-year variance. This was fitted with a sloped cosine function. The residuals from this function were then smoothed, and represent the underlying trend of the original escapement data. The original escapement is displayed with open circles. The running average is the black solid line, the fitted cosine function is also shown. The equation is shown as well as the fitted parameters, and the resulting R^2.

5.3 Results and Discussion

This section will present the down-core data of all the lakes listed in Table 5.1. Kinaskan Lake, which does not receive any salmon, is addressed first, and will be used to evaluate the atmospheric input of contaminants to lakes in the area. This will aid in assessing the distorting influence which the atmospheric contaminant input might have on the salmon signal.

Meziadin and Shuswap lakes will also be discussed in more detail, because they provide interesting insight in the relation process of contaminant data with escapement and δ^{15}N down-core profiles.

Although the data for the other lakes did not show significant relationships between contaminant down-core profiles and escapement or δ^{15}N values, they are still presented individually to permit a complete evaluation of the difficulties associated with this analysis.

5.3.1 Kinaskan Lake

Figure 5.3 shows fluxes of Σchlordane, Σheptachlor, ΣDDT and ΣPCBs. Σchlordane represents the sum of α- and γ- chlordane, both of which experience a clear onset in 1956. The accumulations of γ- chlordane reach a maximum of 0.26 pg cm^{-2} yr^{-1} in 1966, and are only a small fraction of those of α-chlordane (individual fluxes are not shown). α-chlordane accumulations peak a little bit later in 1973 with 8.22 pg cm^{-2} yr^{-1}. Very small concentrations of α-chlordane were detected in earlier sediments (e.g., 1.07 pg cm^{-2} yr^{-1} in sediments dated to 1909), which is probably due to downward diffusion of the chemical in the core.

The Σheptachlor flux in Figure 5.3 includes heptachlor and heptachlor epoxide. Both compounds were not detected in Kinaskan Lake sediments before 1973. Heptachlor epoxide fluxes (individual data not shown) peak in 1973 with 5.53 pg cm^{-2} yr^{-1}, decline afterwards, but start to rise again towards the surface. Heptachlor fluxes (individual data not shown) are smaller, probably because it readily breaks down to heptachlor epoxide, but, interestingly, peak concentrations of heptachlor are observed in the surface sediments (2.85 pg cm^{-2} yr^{-1}). This indicates fresh uses of the pesticide, a possibility that has been suggested recently [73].

ΣDDT in Figure 5.3 is comprised of p,p'-DDE, o,p'-DDT, p,p'-DDD and p,p'-DDT. All of the DDT compounds and metabolites were found in very small amounts (<0.7 pg cm^{-2} yr^{-1}) in sediments dated to 1909 (individual data not shown), which again is attributed to downward diffusion of the chemicals in the core. p,p'-DDT fluxes peak in 1966 (10.12 pg cm^{-2} yr^{-1}), whereas o,p'-DDT and p,p'-DDE have maxima in 1973 (12.11 and 11.17 pg cm^{-2} yr^{-1} respectively). Concentrations of p,p'-DDD are considerably smaller, and peak at the surface (1.84 pg cm^{-2} yr^{-1}).

ΣPCBs (Figure 5.3) include all congeners analyzed in this study (> 100 congeners, see Chapter 2). There is a recent increase of the ΣPCBs in surface sediments, however, the maximum occurs in 1973 with 78.54 pg cm^{-2} yr^{-1}.

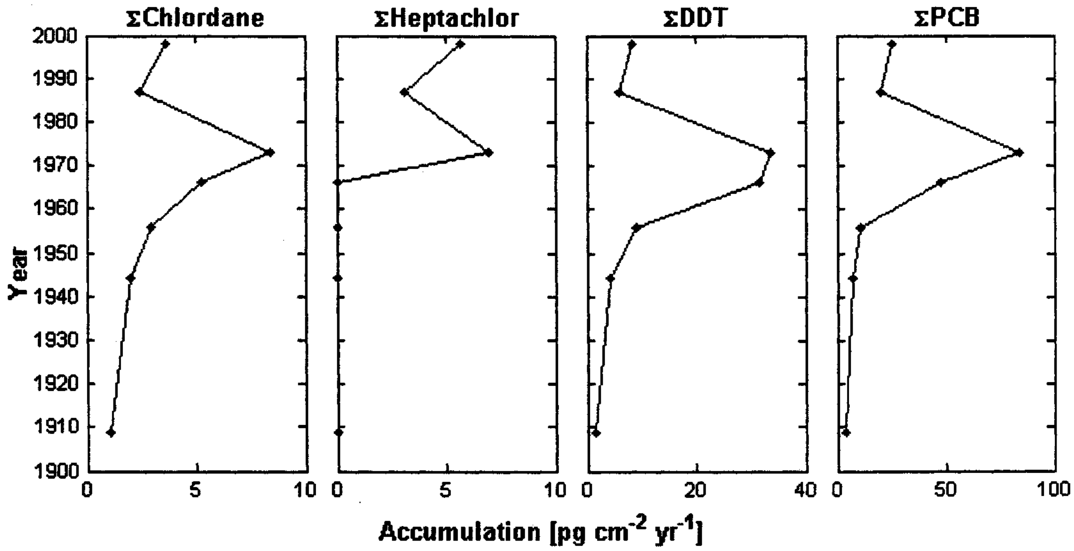

Figure 5.3: Down-core fluxes of sums of chlordane (α- and γ- chlordane), heptachlor (heptachlor and heptachlor epoxide), DDT (p,p'-DDE, o,p'-DDT, p,p'-DDD, and p,p'-DDT), as well as sum PCBs (>100 congeners) in Kinaskan Lake sediments.

Fluxes of individual OC pesticides in Kinaskan Lake sediments are presented in Figure 5.4. Compounds that were not detected include Endrin, Methoxychlor, α-endosulfan, and γ-HCH. Similar to the fluxes in the previous figure (Figure 5.3), the compounds in Figure 5.4 exhibit a maximum around 1970, however, only aldrin is increasing towards the surface (Figure 5.4). Dieldrin is first detected in Kinaskan Lake sediments dated to 1956, whereas the less persistent aldrin can be found for the first time in sediments from 1966 (Figure 5.4). Maximum fluxes of dieldrin reach 3.55 pg cm^{-2} yr^{-1} in 1973, and decline rapidly afterwards. Similar concentrations in Kinaskan sediments dated to 1973 are found for aldrin (3.09 pg cm^{-2} yr^{-1}), however, peak fluxes occur in surface sediments with 6.63 pg cm^{-2} yr^{-1}.

The onset of HCB is earlier compared to that of dieldrin and starts in 1944 (Figure 5.4). Maximum fluxes of HCB occur in Kinaskan Lake sediments dated to 1973 with 101.71 pg cm^{-2} yr^{-1}. The flux of PECB has a very similar pattern to that of HCB and α-HCH, which all have peak concentrations in 1973. However, its maximum concentration at 35.82 pg cm^{-2} yr^{-1} is much lower when compared to the other two. Similar to HCB, fluxes of PECB start to increase in 1944. As mentioned above, the highest accumulation of α-HCH is very similar to that of HCB, with 121.97 pg cm^{-2} yr^{-1} in 1973, but a later onset (starting in sediments dated to 1956).

β-endosulfan was found in very small concentrations in Kinaskan Lake sediments. Fluxes do not exceed 1.5 pg cm^{-2} yr^{-1}, and reach a maximum in 1966. Although endosulfan is still being used, its log K_{OW} is relatively low (see Table 4.3), and it was not very regularly detected in the sediments in this study (also see Chapter 4).

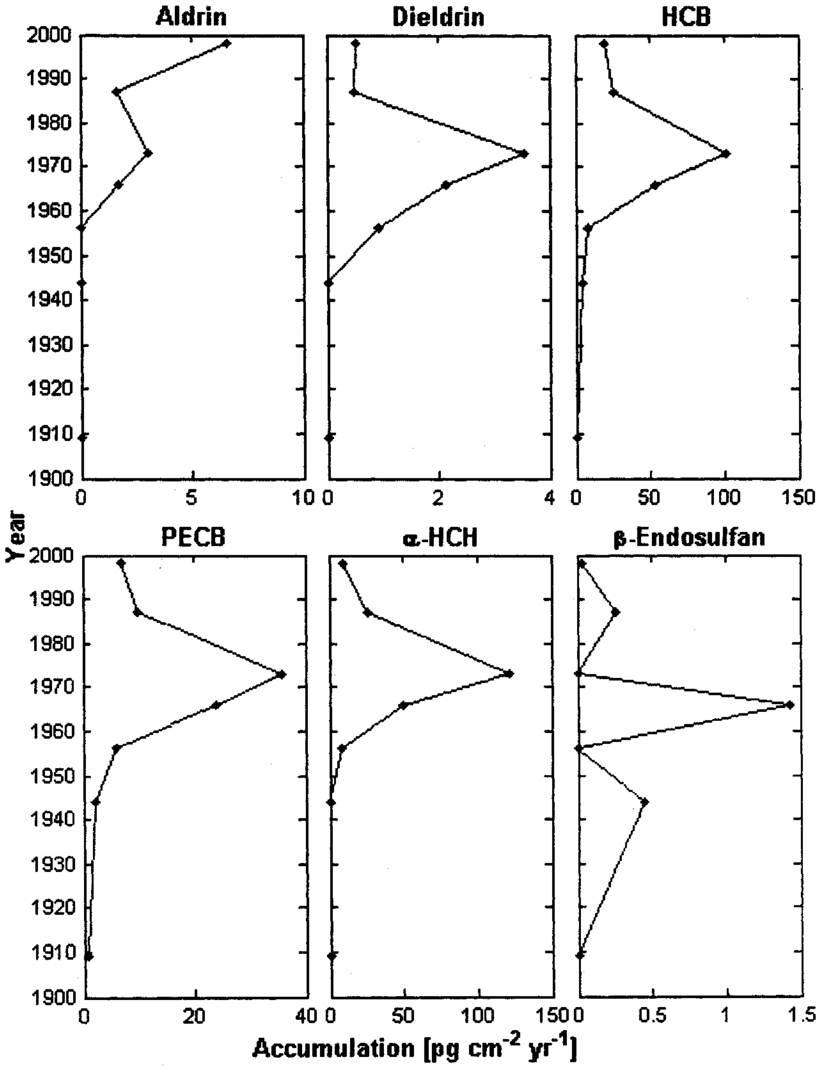

Figure 5.4: Down-core fluxes of aldrin, dieldrin, HCB, PECB, α-HCH and β-endosulfan in Kinaskan Lake sediments.

Overall, down-core profiles of most of the contaminant fluxes in Kinaskan Lake sediments display a very similar pattern: An onset in the mid-1940's to mid-1950's, a peak around 1970, and a following decline (Figure 5.3–5.4). This is what would be expected from the usage history of the POPs investigated here (see Chapter 1), and is very similar to what was found in previous studies. Eisenreich et al. examined two sediment cores from Lake Ontario and found subsurface maxima of PCBs, DDTs, HCHs, heptachlor epoxide and HCB in the mid to late 1960s [39]. Oliver et al. found similar results for DDT, PCBs and HCB in Lake Ontario [117]. A recent study of a lake in the Canadian Arctic observed peak concentrations of PCBs, DDT and chlordane in subsurface slices dated to 1971, which corresponds to the findings presented here [143]. Time differences of contaminant maxima in sediments of different lakes were reported by previous studies and can depend on geographic location of the investigated lake, a finding that supports the global distillation theory [17]. It should also be noted that the time resolution greatly depends on the sedimentation rate and the proximity of dated intervals, which often does not allow for a very precise date determination.

Several of the nutrient related proxies measured in this study also indicate that Kinaskan Lake might have experienced a higher productivity within the last 50 years (Figure 5.5). Percent nitrogen, as well as percent carbon have been increasing since ~1950 (Figure 5.5b, d). The carbon to nitrogen ratio (C/N) has been decreasing within the same timeframe (Figure 5.5h), which indicates a higher lake productivity [107]. Increased lake productivity also often leads to an increase in δ^{15}N and δ^{13}C values, because higher primary production causes a depletion of the carbon and nitrogen pools and therefore result in an elevated fractionation of those nutrients (Wolfe et al., submitted). However, in Kinaskan Lake sediments only δ^{15}N values are increasing, whereas δ^{13}C decreases (Figure 5.5a, c). Compared to carbon, nitrogen is usually the more limiting nutrient in oligotrophic lakes. It might be possible that the nitrogen pool is depleted, but not yet the carbon pool, and δ^{13}C is decreasing because more of the lighter carbon is available. Different algae also have distinguished isotopic signatures, e.g. planktonic algae have lower δ^{13}C values compared to benthic algae [49], and the sediments could contain a higher fraction of planktonic algae. A further indicator for a rising lake productivity in recent decades is the increasing organic matter (%LOI in Figure 5.5e), which was below 6% in the mid 1950's and almost reaches 7% in the surface sediments. Carbonates stayed relatively constant throughout the core, with values between 2.6 and 3%. The sedimentation rate however does not indicate steadily rising fluxes due to increased productivity, instead it displays a distinct peak around 1973 (Figure 5.5g), which is neither reflected by organic matter input, nor by carbonates.

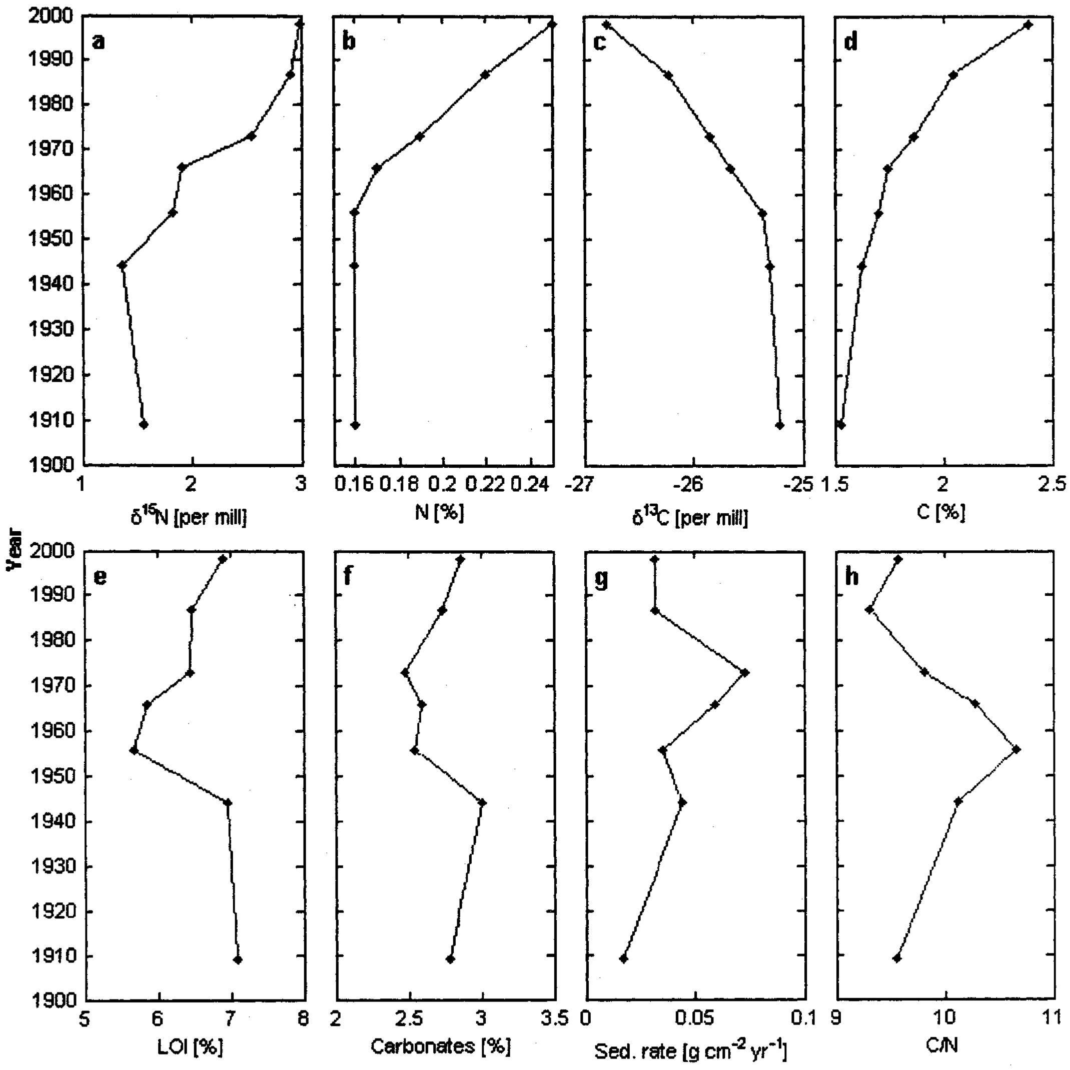

Figure 5.5: Down-core profiles of a, δ^{15}N; b, percent nitrogen; c, δ^{13}C; d, percent carbon; e, percent organic matter (LOI); f, percent carbonates; g, sedimentation rate; h, C/N in Kinaskan Lake.

5.3.2 Meziadin Lake

Meziadin is very suitable to examine the relationship between salmon spawner numbers and other proxies, because it displays a very distinct escapement pattern, which allows for easy comparison with patterns in down-core profiles (Figure 5.6). If sockeye salmon were an important source of contaminants and nutrients (traced by $\delta^{15}N$) to Meziadin Lake in the past, it could be expected that historical escapement and the down-core profiles resemble each other. Indeed, when several down-core profiles are plotted alongside sockeye salmon spawners, similarities in the pattern become apparent (Figure 5.6). Especially the down-core pattern of $\delta^{15}N$ and ΣPCBs exhibit a relatively steady period with little peaks from the late 1950's to the 1980's, a pronounced peak around 1990 (which is skewed toward 2000 in the $\delta^{15}N$ profile), followed by a steep decline and a rise toward recent years. ΣDDT displays instead a distinct peak around 1986, which will be discussed in more detail below. It seems surprising that the ΣDDTs did not record much of the salmon signal during the 1990's, since DDT and its metabolites have the greatest abundance of all the OC pesticides in the salmon samples. However, while the ΣDDTs display only a very slight rise in concentration in the 1990's, two individual DDT compounds (p,p'-DDE and o,p'-DDT, individual data not shown) have more pronounced peaks during this time.

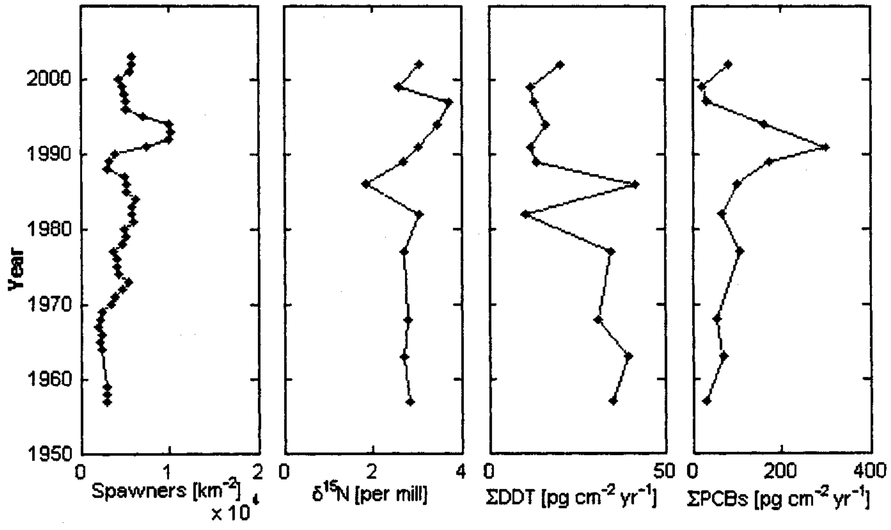

Figure 5.6: Numbers of spawners as reported by DFO and fitted with a 4-year running average, and down-core profiles of $\delta^{15}N$, ΣDDT, and ΣPCBs in Meziadin Lake.

To quantify how well the curves correspond to each other, an initial regression was tried. However, although the curves have a very similar pattern, relations were very weak. To allow for a more direct comparison, the data were then standardized (i.e., the mean was subtracted, and the data was divided by its standard deviation). When the curves where plotted on top of each other, it became apparent that the data could not be related directly, because the curves were slightly shifted (see Figure 5.7 for an example of Meziadin escapement data with the PCB concentration down-core profile). There are several reasons why such shifts can occur. Once the contaminants and nutrients are released by salmon carcasses, they might cycle in the lake before they sediment out and are buried. It was previously found that organic contaminants have a 2–3 times longer residence time in the Great Lakes compared to that of fine particles, which is estimated to be approximately a year [39]. Even after sedimentation, re-suspension can take place in the surface sediments, thus slowing down burial of contaminants and other particles. The deposition history can further be altered by mixing of the surface sediments, as well as by molecular diffusion and possible biotransformation [39]. Finally, systematic errors inherent to data processing and filtering techniques as used with some of the escapement data, or the error associated with the dating process should be considered.

Therefore, to allow for certain shifts in down-core profiles when compared to sockeye spawner counts, one of the curves was moved up (negative delay) and down (positive delay) in relation to the other, and correlated again, until the best fit was found. This process is shown in Figures D.2 and D.3 in the Appendix for the case of escapement and ΣPCB concentration. The resulting best fit achieved an R^2 of 0.795 after a delay of 1.5 years, which is within dating errors (Figure D.3a, b). The significance of the relationship was estimated using a bootstrapping test, because the time-series are autocorrelated (especially the spawner data after the smoothing process). For the bootstrapping, one time series (here the escapement) was randomized, and the regression was repeated. This process was performed a 1000 times, and the resulting R^2 were plotted. The initially measured R^2 was found to fall in the upper 97.5% range of the resulting distribution, therefore indicating a highly significant relationship.

Since down-core data are usually presented as fluxes rather than concentrations, the same process was repeated with ΣPCB accumulation, and although this results in a lower R^2 (0.65), the bootstrapping test indicated the same significance (also see Table 5.2).

When the shifting process was tried for δ^{15}N and escapement, the δ^{15}N curve had to be moved 3 years down to fit the escapement best, and the resulting R^2 was only 0.25. At least partly responsible for the poor fit is probably the dip in δ^{15}N values around the

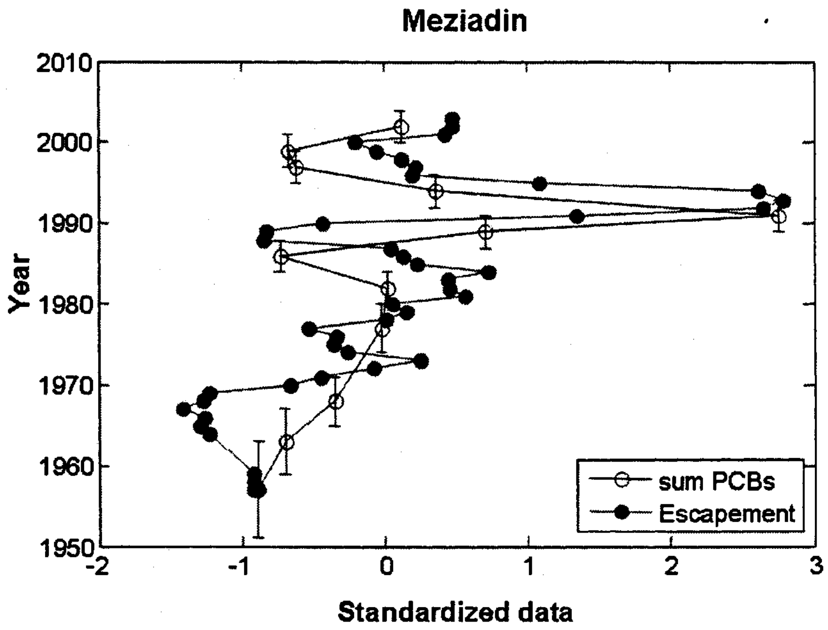

Figure 5.7: Standardized data of Meziadin sockeye escapement and sedimentary ΣPCB down-core concentration. Dating errors are included with the PCB data to visualize a possible shift range.

year 1986. Although this value is very low, it seems to be a true value, since the same dip can be found in δ^{13}C and percent carbonates, and is accompanied by high values in percent nitrogen, percent carbon, organic matter, sedimentation rate and C/N values (Figure 5.8). Apparently an event took place in the watershed around 1986 which diluted the signal of the heavy isotopes by causing a high input of organic matter and nutrients with a light isotopic composition into the lake. The high C/N ratio suggests that the source of the material came from vascular plants [107]. Such an influx of land-based nutrients could be caused by a forest fire or intensive logging activity in the watershed.

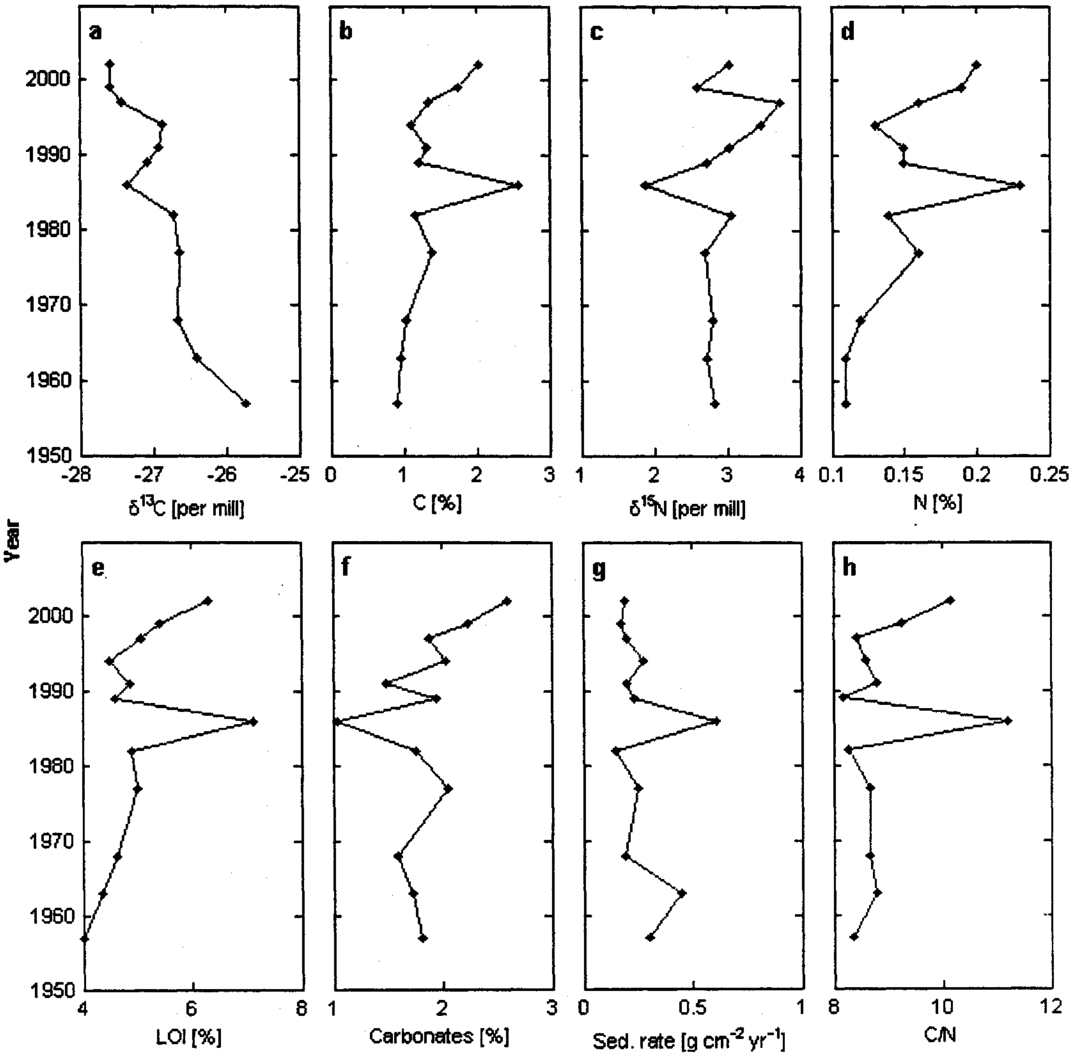

Figure 5.8: Down-core profiles of a, δ^{13}C; b, percent carbon; c, δ^{15}N; d, percent nitrogen; e, percent organic matter (LOI); f, percent carbonates; g, sedimentation rate; h, C/N in Meziadin Lake.

Although it is not apparent from the pattern in the ΣPCB profile, many individual PCBs as well as several organochlorine pesticides also recorded the event in 1986 in their down-core profiles. Most of the OC pesticides have more or less pronounced peaks in 1986, and three compounds (aldrin, dieldrin and Σendosulfan) exhibit high concentrations in 1997 (see Figure D.1 in the Appendix).

The question arises if and how an event, such as that recorded by several proxies in the sediments from 1986, can be distinguished from the salmon signal. Although the peak in salmon abundance occurs at a later date, it can not be determined with absolute certainty when it will be recorded in the sediments, due to the reasons discussed above. A possible solution is the differentiation of contaminants into those that are very abundant in salmon, and those that are not, as described in Chapter 4. The PCBs are especially suited for this task, because there are many congeners with slightly different chemical and physical properties, which result in a slightly different behaviour in the environment.

Closer examination of the down-core profile fluxes of the individual PCB congeners revealed that there are three distinct periods in time where maximum PCB accumulations are recorded. As can be expected from atmospheric deposition, high PCB concentrations are found from the early 1960's to the late 1970's. Several PCB congeners also experience high fluxes in the late 1980's (1986 and 1989), presumably due to the event discussed previously. The third period of high PCB accumulation can be found during the early 1990's (1991–1994), which might correspond to the high spawner abundance around that time. Interestingly, the dominant peak in the ΣPCBs which could be dated to the year 1991, was predominantly caused by high values of PCB congeners 18, 146, and 208-195. However, most of the PCBs that are also abundant in the salmon samples, showed a maximum in 1994. Since salmon abundance peaked between 1991 and 1995, it is very difficult to determine which of the contaminants truly represent the salmon signal in the sediments, especially if the contaminant pattern in the salmon should have changed over time, as discussed in the previous chapter. If it could be assumed that the contaminant pattern in the salmon did not change over time, a 'true' salmon signal could be achieved by taking the ratio of contaminants abundant in salmon to the contaminants that represent the 'non-salmon' input to the lake. This was tried by taking the sum of 'salmon PCBs' (PCB congeners 101, 153-132-105, and 138-163, total abundance in salmon samples 26%) and dividing it by the sum of 'non-salmon PCBs' (PCB congeners 22, 44, and 100, total abundance in salmon samples <4%). Sums were taken to avoid the incident of non-detects in any given sample. Figure 5.9 shows the down-core profiles of the 'salmon PCBs', the 'non-salmon PCBs', and their ratio which represents the salmon signal, provided that the contaminant pattern in the salmon did not change.

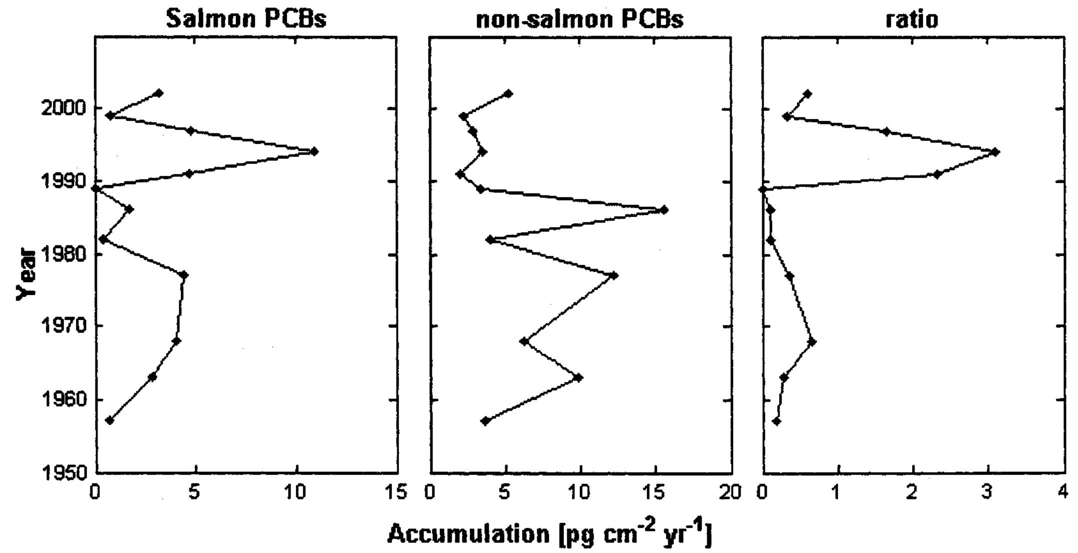

Figure 5.9: Down-core profiles of 'salmon PCBs' (PCB congeners 101, 153-132-105, and 138-163), 'non-salmon PCBs' (PCB congeners 22, 44, and 100), and their ratio (the resulting salmon signal) for Meziadin Lake.

Figure 5.9 illustrates clearly the differences between the pattern of 'salmon PCBs' versus that of 'non-salmon' PCBs. The 'salmon PCBs' show a much smaller, broader shaped peak between 1960 and 1980 compared to the 'non-salmon PCBs', whose peak around this time has two maxima (in the early 1960's and late 1970's), and is generally much higher. The opposite is true for the peak around 1986, which can be found in both groups, but is much higher for the 'non-salmon PCBs'. The again reversed effect is observed for the peak in 1994, which is very pronounced in the 'salmon PCBs', but rather small for the 'non-salmon PCBs'. Both groups show a recent increase in their fluxes. The ratio between the two groups then displays a very pronounced peak in 1994, almost no peak in 1986, and a very small, broad peak between the 1960's and 1980's.

Table 5.2 summarizes the results of shifting processes with subsequent relations for fluxes of ΣPCBs, 'salmon PCBs', 'non-salmon PCBs', and the ratio of the latter two ('salmon signal') versus escapement and δ^{15}N. The delay in years indicates how much the second time-series was shifted up (i.e., a delay forward in time, indicated by negative numbers in the table) or down (i.e., delayed backward in time, indicated by positive numbers in the table). The R^2 is given for the relationship as well as the F-statistic probability, although the significance does not take into account autocorrelation. Therefore, the bootstrap R^2 value is added, at which level the upper 97.5% threshold is reached. If the R^2 of the relatinship is above this value, it indicates that the significance is indeed at a level of $p<0.05$.

The results visualize that the 'salmon PCBs' and the 'salmon signal' require the least time-shift to attain a proper relationship with escapement, which is not surprising since the extent of the shift is predominantly determined by the location of the maximum peak. As stated above, a dominating peak can be found in all contaminant down-core profiles: one in the early 1990's (probably caused by salmon), and one in the late 1980's (apparently due to an event in the watershed). The 'salmon PCBs' recorded a major peak in the early 1990's, and therefore only a small shift is needed to achieve the best fit. However, since the 'non-salmon PCBs' mainly recorded the peak in the late 1980's, a larger shift between contaminant fluxes and escapement is required for those contaminants. Nevertheless, the resulting regression is not significant (Table 5.2).

Overall, the best fit of the escapement is narrowly achieved with the ΣPCBs, closely followed by that of the 'salmon signal' (Table 5.2). Evidently, the atmospheric deposition or other contaminant inputs are not overlaying the salmon signal of the ΣPCBs in a very significant way, which would confirm salmon as the major source of PCBs to Meziadin Lake sediments. The comparable poorer fit of the 'salmon PCBs' might be due to a change in congener patterns in the salmon over time. Since the ΣPCBs values consist of all the congeners, they also include PCB congeners that had a higher abundance in salmon in the past and are therefore less susceptible to the effects of changing congener patterns in the respective source.

Escapement and $\delta^{15}N$ could not be related successfully, probably because the event in the late 1980's, which had a diluting effect on the $\delta^{15}N$ values, distorted the $\delta^{15}N$ salmon signal considerably. Nevertheless, $\delta^{15}N$ still achieved significant relationships with the PCB down-core profiles. Here, the best fit is attained by the 'salmon signal', with a shift of 1.5 years (Table 5.2), followed by that of the ΣPCBs, although the shift is larger with 3.5 years. The salmon PCBs have a slightly worse R^2 compared to that of the ΣPCBs, however, the time delay is the same as for the 'salmon signal' (1.5 years). Basically no relationship can be found with 'non-salmon PCBs' and $\delta^{15}N$ (Table 5.2).

No successful regressions with ΣDDT or its metabolites either with escapement or with $\delta^{15}N$ were possible, and they were therefore not included in the table.

Table 5.2: Shifting process and relations for fluxes of ΣPCBs, 'salmon PCBs', 'non-salmon PCBs', and the ratio of the latter two ('salmon signal') versus escapement and $\delta^{15}N$ in Meziadin Lake.

Regression type	Delay (Years)	R^2	F-statistic probability	Bootstrap R^2 at 97.5%
ΣPCB vs. esc.	1.5	0.653	0.0026	0.53
ΣPCB vs. $\delta^{15}N$	3.5	0.564	0.01	0.36
'salmon PCBs'[a] vs. esc.	0	0.445	0.018	0.43
'salmon PCBs' vs. $\delta^{15}N$	1.5	0.533	0.011	0.52
'non-salmon PCBs'[b] vs. esc.	6	0.218	0.17	N/A[c]
'non-salmon PCBs' vs. $\delta^{15}N$	10	0.037	0.65	N/A[c]
'salmon signal'[d] vs. esc.	0	0.651	0.0015	0.44
'salmon signal' vs. $\delta^{15}N$	1.5	0.705	0.0012	0.42

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[a] Sum of PCB congeners 101, 153-132-105, and 138-163.

[b] Sum of PCB congeners 22, 44, and 100.

[c] Bootstrap was not performed.

[d] Ratio of 'salmon PCBs' to 'non-salmon PCBs'.

5.3.3 Shuswap Lake

Comparisons between down-core pattern in the sediments and escapement for Shuswap Lake are somewhat impeded by the highly variable spawner abundance, as described in the Methods-section earlier in this chapter. Spawner abundance in Shuswap Lake fluctuates not only with the 4-year spawner cycle, but also with a decadal, climate related cycle (see Figure 5.2). Total spawner numbers reached a maximum in 2002 with more than 4.6 million spawners (~13,000 per km^2), but the average spawning number is around 560,000 (~1,600 per km^2). It is therefore not surprising that the translation of this signal into the sediments is rather difficult to reconstruct, as indicated by Figure 5.10.

Although the down-core profiles of $\delta^{15}N$ and ΣPCB concentration are very similar, and are also positively related (see Table 5.3), there is no apparent resemblance of either ΣPCB concentration, or $\delta^{15}N$ down-core profiles with escapement. It could be assumed that the from the escapement data extracted trend does not capture the salmon signal which is preserved in the sediments. Generally, the salmon signal is also rather small compared to the effect of other factors, as can be seen from the down-core profiles of

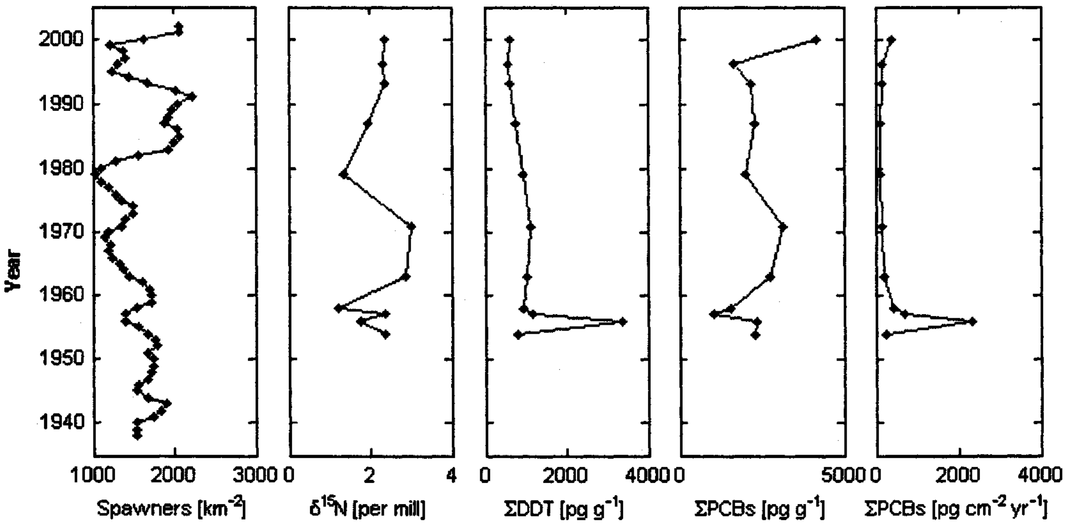

Figure 5.10: Shuswap Lake escapement pattern as derived from the fitting process, and down-core profiles of δ^{15}N, ΣDDT and ΣPCB concentrations, as well as ΣPCB accumulation.

ΣDDT and ΣPCB flux in Figure 5.10. A very high sedimentation rate around 1956–57 produces extremely high values of some contaminant fluxes, as well as concentrations, and causes the virtual disappearance of the other pattern observed in the contaminant concentration profiles. Similar to the event in Meziadin Lake, this high sedimentation rate value is credible, because it is accompanied by responses of the other proxies, such as percent carbonates, LOI, carbon and nitrogen, around the same time (Figure 5.11). This time however the signal seems to be of inorganic nature, since percent organic matter decreases, while carbonates increase. Percent nitrogen and carbon also decline, which probably caused a higher fractionation of the isotopes, thus resulting in heavier δ carbon and nitrogen values.

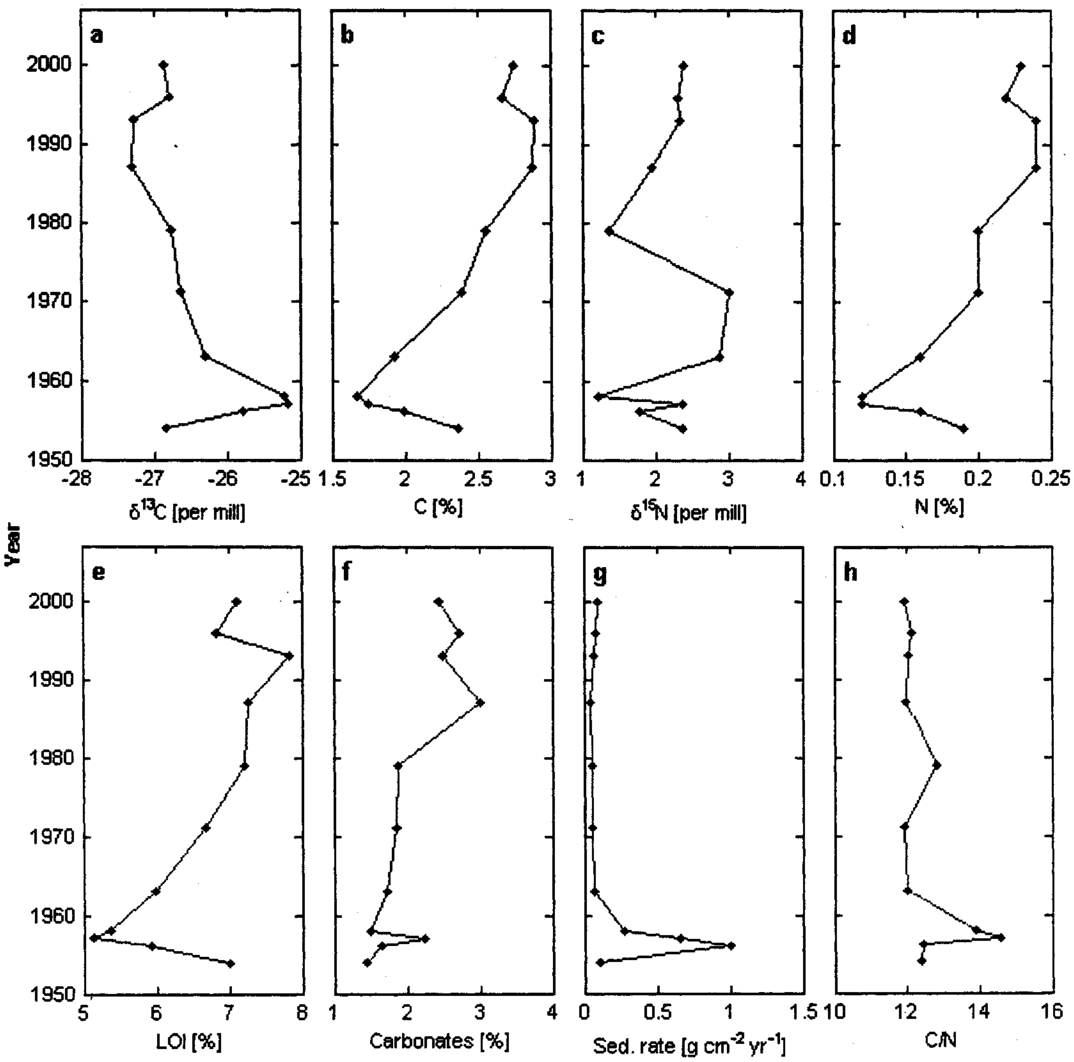

Figure 5.11: Down-core profiles of a, δ^{13}C; b, percent carbon; c, δ^{15}N; d, percent nitrogen; e, percent organic matter (LOI); f, percent carbonates; g, sedimentation rate; h, C/N in Shuswap Lake.

OC pesticide fluxes show mostly the same pattern as observed with the ΣPCBs, with a strong peak in the late 1950's, which diminishes any pattern that might exist otherwise (data not shown). OC pesticide concentration down-core profiles also often display pronounced peaks around 1957, however, in some cases broader peaks are visible between 1960 and the 1970's, as well as around 1990 (Figure D.5 in the Appendix). HCB, PECB and Σendosulfan are more or less continuously rising to the surface.

Table 5.3 summarizes the shifting and regression results for the PCBs and δ^{15}N. Since fluxes were highly influenced by the event in 1956–1957, concentrations were used rather than fluxes. ΣPCBs and 'salmon PCBs' showed the best relationships, followed by the 'non-salmon PCBs'. Since the 'non-salmon PCBs' could be related successfully to δ^{15}N, they also seemed to follow somewhat the salmon input into the lake, which might indicate that salmon were the most important source of PCBs to the lake. It is therefore not surprising that the ratio of the 'salmon PCBs' to the 'non-salmon' PCBs ('salmon signal') did not show a significant relationship with δ^{15}N.

For the DDT's, only o,p'-DDT displays a profile which resembles somewhat that of δ^{15}N (individual data not shown), but a regression proved to be significant only after a delay of -9.5 years, and was therefore not included.

Since no relationships with escapement were significant, they were also not included in the table.

Table 5.3: Shifting process and relations for down-core profiles of ΣPCBs, 'salmon PCBs', 'non-salmon PCBs' concentrations, and the ratio of the latter two ('salmon signal') versus δ^{15}N in Shuswap Lake.

Regression type	Delay (Years)	R^2	F-statistic probability	Bootstrap R^2 at 97.5%
ΣPCB vs δ^{15}N	1	0.686	0.003	0.35
'salmon PCBs'[a] vs δ^{15}N	1	0.662	0.0042	0.40
'non-salmon PCBs'[b] vs δ^{15}N	1.5	0.434	0.0382	0.43
'salmon signal'[c] vs δ^{15}N	-6	0.30	0.2034	0.6

---

[a] Sum of PCB congeners 101, 153-132-105, and 138-163.

[b] Sum of PCB congeners 22, 44, and 100.

[c] Ratio of 'salmon PCBs' to 'non-salmon PCBs'.

5.3.4 Bowron Lake

Comparisons between trends in down-core data and escapement for Bowron Lake are complicated by its relatively low sedimentation rate, which translates into a low resolution of the down-core profiles. The task is further obscured by the variable salmon abundance numbers, and the uncertainty of the signal appearance they might leave in the sediments. Figure 5.12 displays total sockeye salmon spawner numbers as provided by DFO, as well as the 4-year running average that was fitted through the data. Some high spawner numbers that occurred between 1960 and 2000 are not expressed in the averaged dataset, because of the very low numbers in subdominant and nondominant years that followed each dominant year. Similar to what was found for Shuswap Lake, it is therefore difficult to determine whether the down-core profiles of δ^{15}N and the contaminants capture past spawner numbers in the sediments.

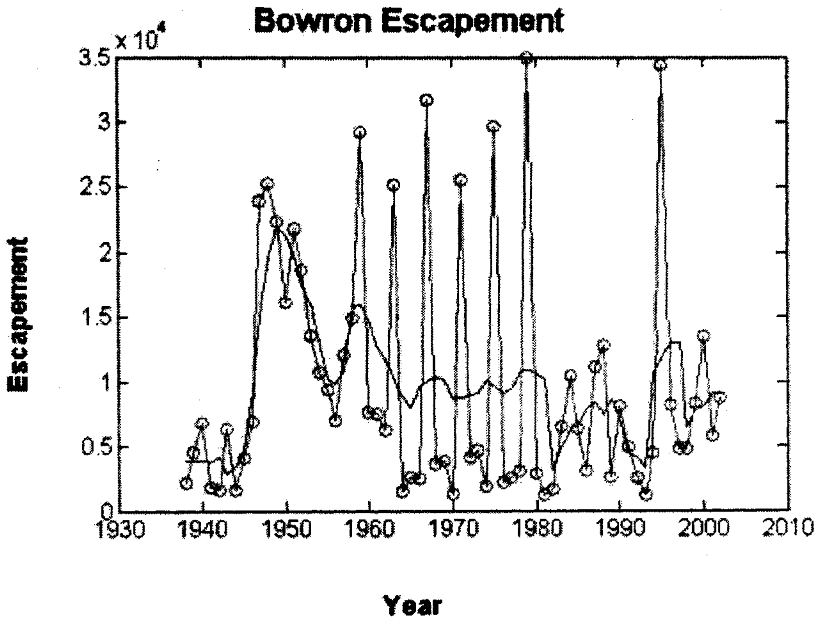

Figure 5.12: Total numbers of sockeye salmon spawners (open circles) and 4-year running average (solid line) in Bowron Lake.

The averaged escapement data and down-core profiles of δ^{15}N, as well as ΣDDT, and ΣPCB fluxes are plotted in Figure 5.13. There are no apparent similarities between escapement data and the down-core profiles, and it is therefore not surprising that no significant relationships could be found. Due to the limiting number of values, the

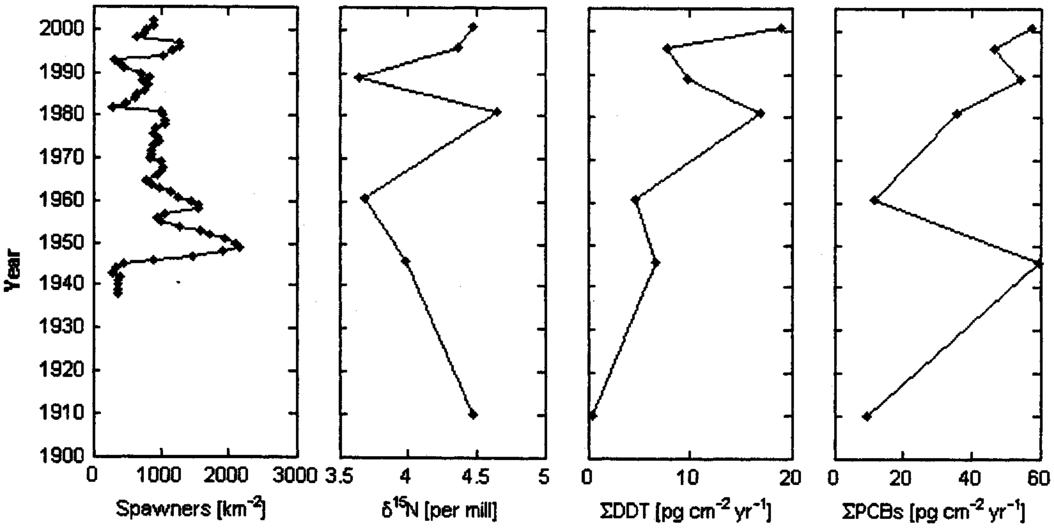

Figure 5.13: Total number of spawners as reported by DFO and fitted with a 4-year running average, and down-core profiles of δ^{15}N, ΣDDT, and ΣPCB fluxes for Bowron Lake.

pattern in the down-core profiles are often shaped by very abrupt peaks. Although the cause remains unclear, both profiles of δ^{15}N and ΣDDT have a very distinct peak around 1980, which is followed by a decline and a further increase toward the surface (Figure 5.13). The only difference between the two curves is a higher value for δ^{15}N in 1910, whereas ΣDDT values decline (which is in accordance with the production and usage of the contaminant). A regression of the two down-core profiles is very significant when the δ^{15}N data is shifted upward (delay of -3.5 years, $R^2 = 0.908$, $p = 0.003$, bootstrap value at 97.5% = 0.76.). However, the PCB data does not reflect the same pattern, and regressions with ΣPCBs or selected congeners were not successful. The maximum in the ΣPCB flux around 1946 is probably related to a peak in the sedimentation rate, and possibly the relatively high escapement at that time (Figure 5.14). Nevertheless, a clear indication of the origin of the high values in the two profiles of ΣPCBs and sedimentation rate remains uncertain, since none of the other proxies seem to be recording the event. Percent organic matter (LOI) and C/N instead indicate a peak in the late 1980's, which is also reflected somewhat in the ΣPCB accumulation, but is accompanied by a decrease in δ^{15}N, percent nitrogen, and also ΣDDT values (Figures 5.14 and 5.13). Although most of the other OC pesticides had either very low fluxes, or were rarely detected in the sediments of Bowron Lake, a common feature is a more or less steady increase since the

1960's (see Figure D.6 in the Appendix). Very similar to what was observed in Kinaskan Lake, Bowron Lake sediments showed overall increasing trends of percent carbon and organic matter, which was again associated with a decrease in δ^{13}C (Figure 5.14). As discussed previously, this might point toward a increasingly higher lake productivity, and a related higher net absorption of contaminants in the sediments.

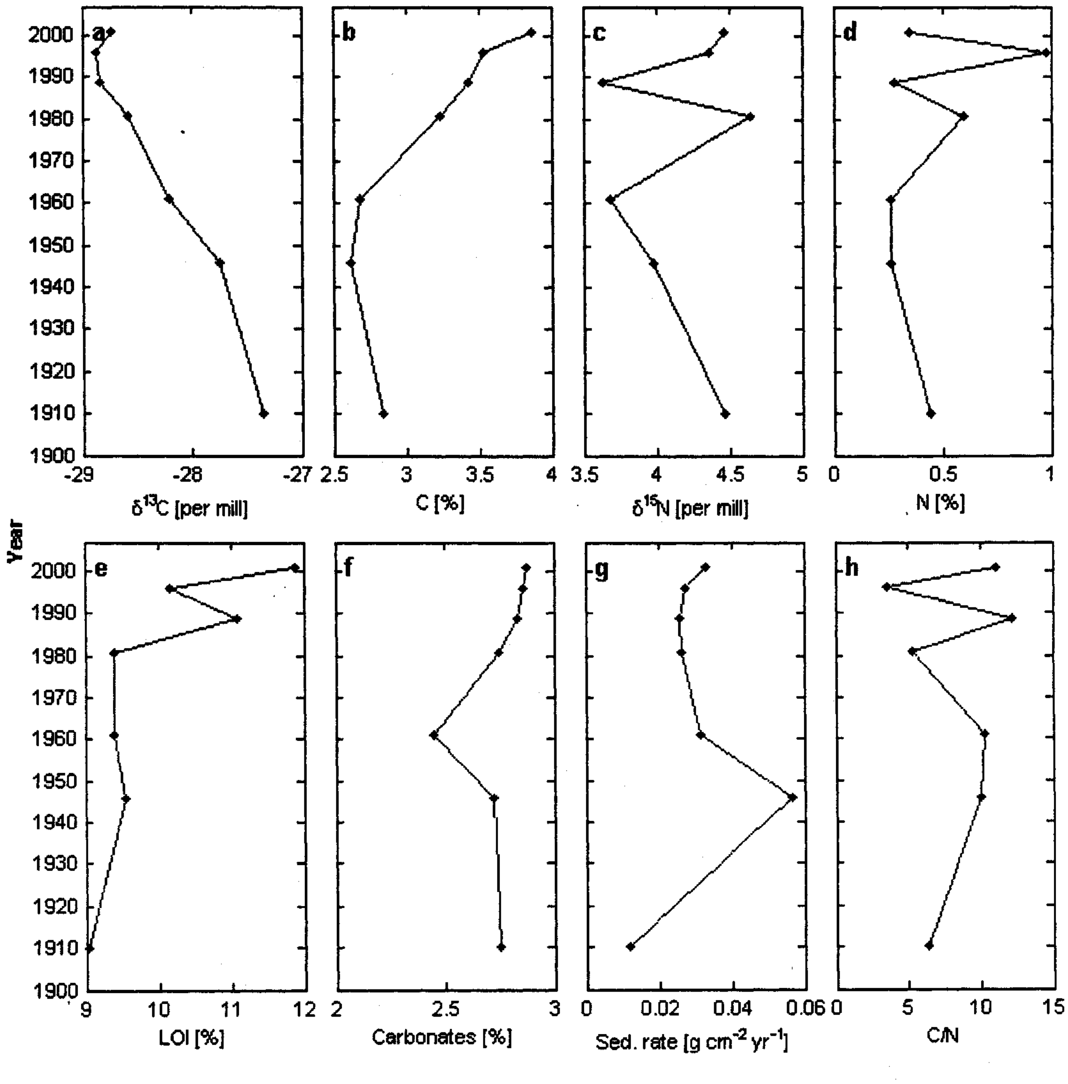

Figure 5.14: Down-core profiles of a, δ^{13}C; b, percent carbon; c, δ^{15}N; d, percent nitrogen; e, percent organic matter (LOI); f, percent carbonates; g, sedimentation rate; h, C/N in Bowron Lake.

5.3.5 Quesnel Lake

Quesnel Lake will not be discussed in detail due to its very low sedimentation rate, which resulted in an extremely low resolution in the down-core profiles. As can be seen in Figure 5.15, only 4 datapoints are available for interpretation within the last century. Any form of detailed comparison between spawner data and down-core profiles is thus not possible. It can be generally noted that escapement as well as several down-core profiles show an increasing trend toward recent years, such as several of the contaminants, as well as percent carbon, percent nitrogen, δ^{15}N and organic matter (see Figure 5.15, and Figures D.7 and D.8 in the Appendix). Similar to what was seen in the other lakes, δ^{13}C is decreasing during the same time. Fluxes of contaminants in Quesnel Lake were rather low, and similar to what was found in Shuswap Lake, many OC pesticides were rarely detected. Most of the contaminants that were detected display and increase toward the surface. ΣDDT and ΣPCB fluxes also seem to be recording a higher deposition around 1960 (Figure 5.15).

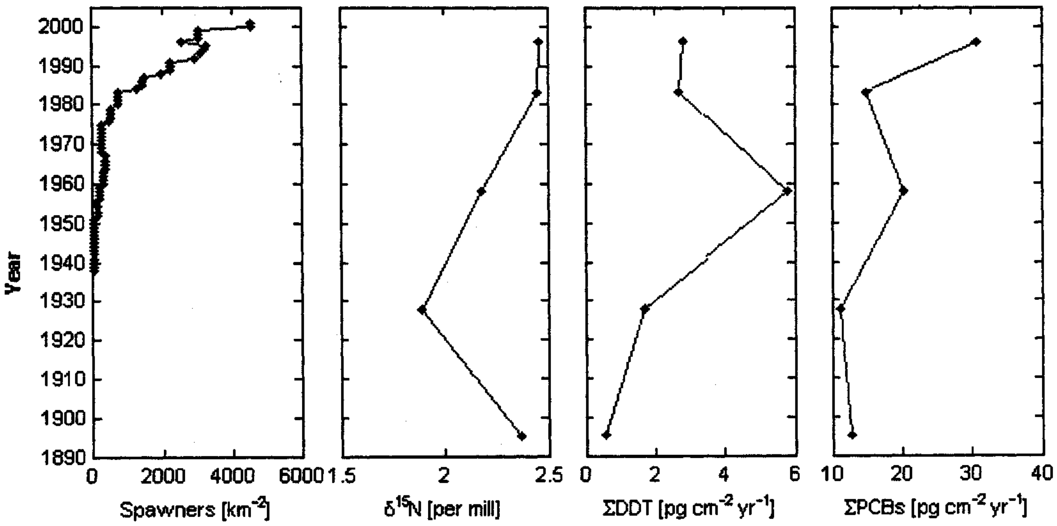

Figure 5.15: Total number of spawners as reported by DFO and fitted with a 4-year running average, and down-core profiles of δ^{15}N, ΣDDT, and ΣPCB fluxes for Quesnel Lake.

5.3.6 Fraser Lake

The two cores that were taken in Fraser Lake are very different, as mentioned already in Chapter 3. The discrepancy arises because of the different coring locations: Core 1 was taken in the centre of the lake, while Core 2 was taken in the southwest basin, closer to the city of Fraser, and to the outflow of Stellako River, where the salmon come in to spawn (Figure D.9 in the Appendix). Core 1 has a very small sedimentation rate, which results in only three values in the down-core profiles within the range of historic salmon counts (see Figure 5.16). Comparisons between pattern of past escapement and down-core profiles are thus not possible for Core 1. Core 2 has much higher sedimentation rates, but contaminant values were found to be extremely high in the surface sediments, as well as in greater depths (below the last dated year of 1933). It was therefore decided to remove this core completely from the data analysis.

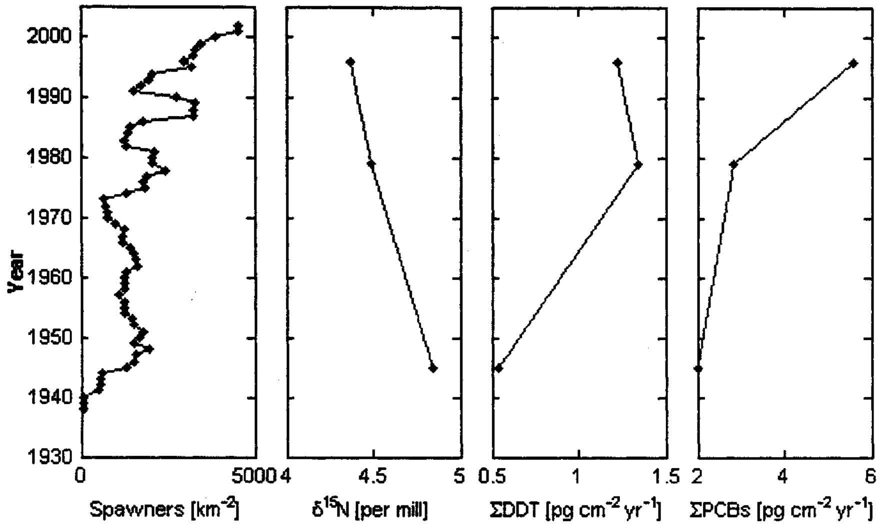

Figure 5.16: Total numbers of spawner as reported by DFO and fitted with a 4-year running average, and down-core profiles of δ^{15}N, ΣDDT, and ΣPCB fluxes for Fraser Lake, Core 1.

5.3.7 Red Lake

Red Lake is the highest sockeye salmon receiving lake (on a per area basis) in this study, and is historically also one of the most consistent sockeye producing lakes on Kodiak

Island. The Alaska Department of Fish and Game monitored escapement especially in recent years closely by sonar estimates or weir counts, and spawning returns are carefully managed to ensure the system is not over- or underutilized. Probably due to the careful management, salmon returns in Alaskan lakes are not as heavily influenced by the 4-year life cycle compared to lakes in B.C., and the 4-year running average displays the general trend of sockeye abundance very well (Figure 5.17). However, there was no escapement data available for Red Lake between 1953 and 1963.

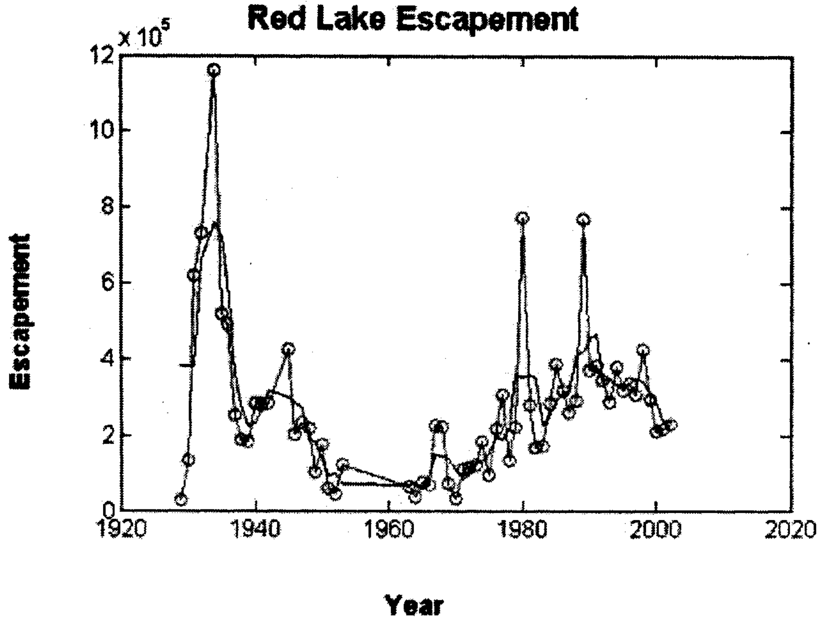

Figure 5.17: Sockeye salmon spawner numbers for Red Lake as provided by the Alaska Department of Fish and Game (open circles) and the 4-year running average that was fitted through the data (solid line).

Comparisons between historical escapement and the down-core profile of δ^{15}N clearly show that δ^{15}N values do not track past salmon abundance in the sediments of Red Lake (Figure 5.18). The negative relationship between the two proxies has been observed in earlier cores (Bruce Finney, University of Alaska Fairbanks, personal communication), but the mechanisms at work have not yet been identified. The observation of lighter δ^{15}N signals in sediments of remote lakes due to anthropogenic nitrogen deposition as reported by Wolfe et al. [150] is improbable due to the intensity of the salmon signal in nursery lakes. It is also usually assumed that denitrification is not an issue in salmon nursery lakes, because these lakes are mostly oligotrophic and are thus not likely to reach anoxic conditions [82]. However, maybe the high density of spawners in Red Lake, whose carcasses can be expected to decompose very slowly at greater depths [82], could in fact contribute to conditions at the sediment-water interface that favour denitrification.

The high spawner numbers are also assumed to be responsible for the high organic matter content in Red Lake, which was already shown to be related to spawner densities in Chapter 4 (see Figure D.11 in the Appendix for down-core profiles of LOI and the other proxies). C/N ratios are relatively low in Red Lake sediments and indicate that nutrient input from vascular plants in the watershed is not a major contributor to the lake. Similar to what was already reported for the other lakes in this study, percent carbon and nitrogen are increasing, while their δ values are declining (Figure D.11).

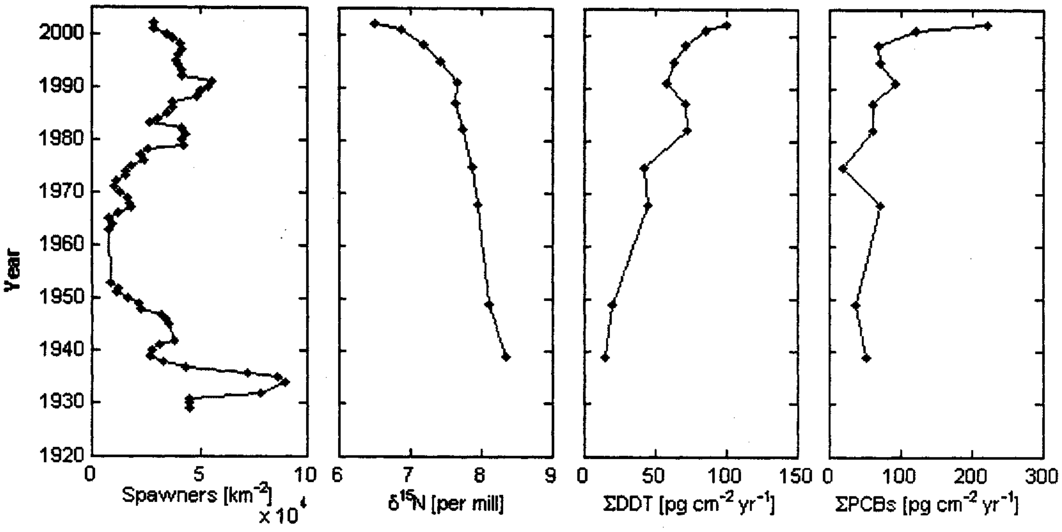

Figure 5.18: The 4-year running average of sockeye salmon escapement, and down-core profiles of δ^{15}N, ΣDDT, and ΣPCB fluxes for Red Lake.

The escapement pattern between 1960 and recent years has been relatively steady and without striking features which could be easily compared to contaminant down-core profiles. Generally, spawner numbers have been increasing since 1960, but there is a recent decline. Down-core profiles of ΣDDT, and ΣPCB fluxes are also increasing since the 1940's, but similar to what was found in the other lakes, recent fluxes are not declining. Small peaks in spawner abundance during the 1980's and early 1990's may be reflected by the small peaks in some of the contaminant down-core profiles (which is more pronounced in ΣHCH, see Figure D.10 in the Appendix). Regressions with escapement and ΣPCB fluxes were positive but very weak after a shift of 1.2 years ($R^2 = 0.252$), and somewhat stronger for escapement and ΣDDT (shift = 1.2 years, $R^2 = 0.404$, $p = 0.066$, bootstrap R^2 value at 97.5% = 0.45).

5.3.8 Upper Olga Lake

Figure 5.19 displays the 4-year running average of sockeye salmon numbers, and down-core profiles of $\delta^{15}N$, ΣDDT, and ΣPCB fluxes for Upper Olga Lake. Unfortunately no spawner numbers were available between 1958 and 1970, but the dip in $\delta^{15}N$ values around that time might suggest that spawner abundance in those years was in fact low. A regression between escapement and the $\delta^{15}N$ down-core profile was positive ($R^2 = 0.403$) after a shift of -3.5 years (i.e., the escapement was shifted upward), but the regression is then based on only 5 values, which does not allow for reliable conclusions regarding the significance of the relationship. Contaminant down-core profiles show mostly maxima at the surface, a dip around 1990, and often relatively broad shaped peaks between 1960 and 1980 (see Figure 5.19 for fluxes of ΣDDT, and ΣPCB and Figure D.12 in the Appendix for fluxes of selected OC pesticides). A clear relationship between contaminant down-core profiles and escapement or $\delta^{15}N$ is not visible.

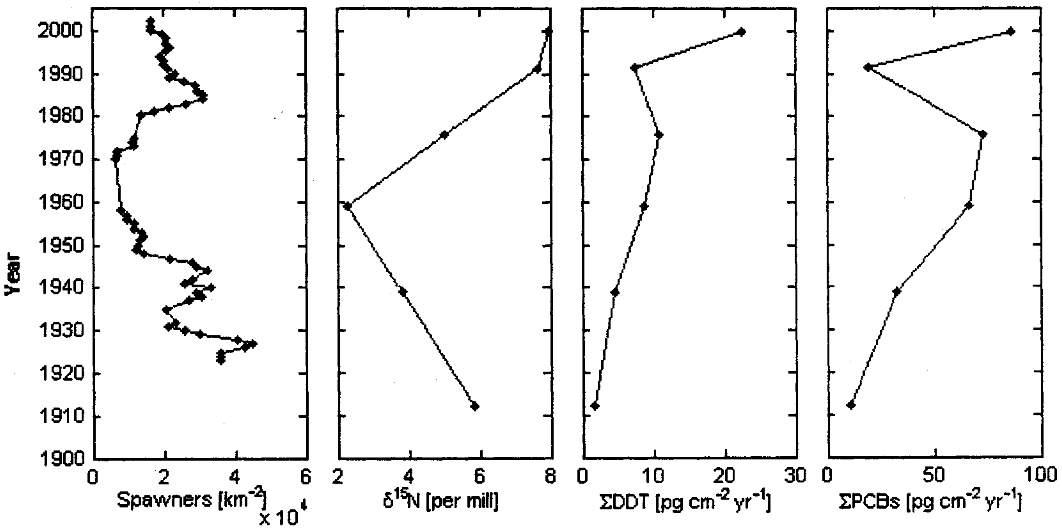

Figure 5.19: The 4-year running average of sockeye salmon escapement, and down-core profiles of $\delta^{15}N$, ΣDDT, and ΣPCB fluxes for Upper Olga Lake.

Percent carbon and nitrogen down-core profiles show a rising trend in Upper Olga sediments, similar to what was seen in the other lakes in this study, and δ^{13}C values are also declining (Figure D.13 in the Appendix). In general, δ values in Upper Olga Lake sediments are relatively heavy and C/N values low compared to other lakes. The C/N ratios are also very steady and vary only between values of ~6.6 to 6.9. This might indicate that salmon are the prevalent source of nutrients to this lake, and input from the watershed is probably very low.

5.3.9 Frazer Lake

Contaminant down-core profiles could not be successfully related with escapement in Frazer Lake, although higher concentrations are found around 1986 for many POPs, which correspond to the increase in spawner abundance (Figure 5.20 and Figure D.14 in the Appendix). However, while recent salmon abundance seems to be decreasing, all measured contaminants display very strong increases in concentrations toward the surface. This trend can also be found in total mercury values, which were measured in freeze dried sediments from a core taken in 1998. Surprisingly, total mercury is lacking any peak that could be related to the increased escapement during the 1980's. ΣDDT and some of the other OC pesticides seem to record the increased salmon abundance in the 1980's, and additionally show sub-surface peaks around 1970, which are most likely caused by higher atmospheric input (Figure 5.20 as well as Figure D.14 in the Appendix).

ΣPCB down-core fluxes, which do not show a noticeable increase in concentration around 1970, were positively related to δ^{15}N values, but the relationship was not significant ($R^2 = 0.323$, delay = -2 years, $p = 0.11$, bootstrap R^2 at 97.5% = 0.36). The most likely reason for the poor relationship is the steep increase of the ΣPCB values in recent years.

It should be mentioned that while the increase in contaminant values toward the surface has been seen in many of the other lakes, ΣPCB concentrations were surprisingly high in surface sediments from this core, and exceeded the previously reported values. One value at a depth dated to 1900 also had ΣPCB concentrations above the background concentration. It is therefore possible that contamination occurred during processing of the core.

When comparing the smoothed historical escapement with the down-core profile of δ^{15}N in this study, the similarities become apparent. A regression of the two time series

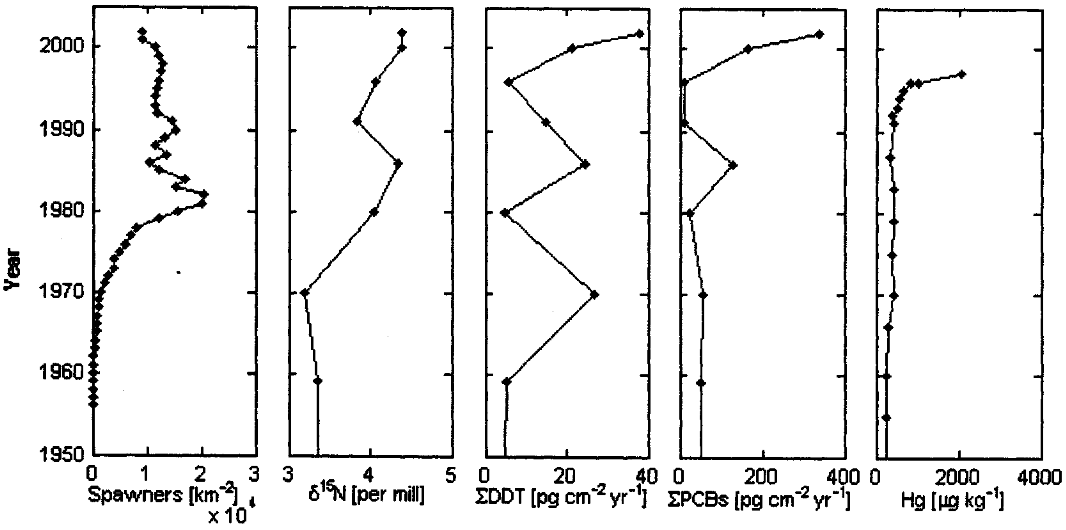

Figure 5.20: The 4-year running average of sockeye salmon escapement, and down-core profiles of δ^{15}N, ΣDDT, and ΣPCB fluxes, as well as total Hg in Frazer Lake sediments.

is very significant after a delay of -3 years (i.e. the escapement is moved upward), with an R^2 of 0.825 ($p = 0.0018$, bootstrap R^2 at 97.5% = 0.62). The fertilization of Frazer Lake during the late 1980's and early 1990's had apparently no distorting effect on the δ^{15}N values, although it probably caused the observed peak in the sedimentation rate dated to that time (Figure D.15 in the Appendix). Since fertilizers usually have depleted δ values, a diluting effect could be expected if significant amounts are being added to the system. The δ^{15}N values experience a short decline around 1990, but it is not apparent if the cause is rather the decrease in salmon abundance. The high escapement numbers in the years before likely diminished any previous depleting impact on the sedimentary δ^{15}N values.

5.3.10 Karluk Lake

Most of the contaminant down-core profiles in Karluk Lake do not show any resemblance to the historical escapement pattern. As seen in Frazer Lake, down-core fluxes of ΣPCBs are mostly defined by the huge increase in contaminant concentration in the surface sediments, which are also higher than what was previously reported. Although ΣPCB concentrations in greater depth are declining as expected, a higher value in ΣDDT concentrations at a depth dated to 1920 could be related to contamination during processing of the sediments.

Although total mercury data, which was analyzed from freeze dried sediments cored in 1998, displays peaks that correspond to high salmon abundance in the early 1950's and the late 1970's, there was no significant relationship. The reason might be the disproportional large increase of mercury concentrations compared to the relatively small rise in spawner abundance.

Similar to Frazer Lake, Karluk has been fertilized from 1986 to 1990, but while the fertilizer application to Frazer Lake was relatively large, the application to Karluk Lake was rather modest [56], and did not result in changes of sedimentation rates as seen in Frazer Lake (Figure D.17 in the Appendix). However, although escapement numbers increased during the period of fertilization, $\delta^{15}N$ values stayed low (Figure 5.21), which was previously attributed to the diluting effect of the fertilization by Gregory-Eaves et al. [56]. Nevertheless, the down-core profile of $\delta^{15}N$ closely matches the pattern of historical salmon abundance, and was confirmed by a regression of the two time-series (R^2 of 0.801 after a delay of -5 years, p = 0.001, bootstrap R^2 at 97.5% = 0.46).

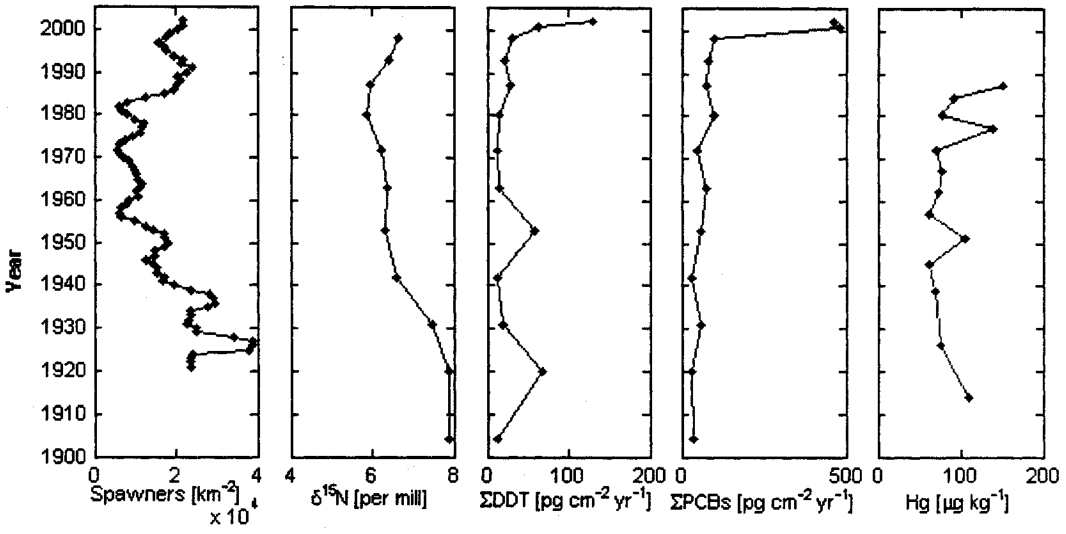

Figure 5.21: The 4-year running average of sockeye salmon escapement, and down-core profiles of $\delta^{15}N$, ΣDDT, and ΣPCB fluxes, as well as total Hg in Karluk Lake sediments.

The down-core fluxes of several OC pesticides display a pronounced peak in 1987, which might be related to spawner abundance or the previously discussed fertilization of Karluk Lake, and a more or less distinctive peak in the mid-1950's (Figure D.16 in the Appendix). Almost all of the OC-pesticide fluxes are also increasing toward the surface. The frequently observed increase of percent carbon, nitrogen and organic matter, accompanied by a decline in δ^{13}C values is also visible in Karluk Lake sediments (Figure D.17).

5.4 Summary

The objective of this part of the thesis was to investigate whether sockeye salmon can be identified as a historical source of contaminants to 9 nursery lakes. Since δ^{15}N is a widely accepted tracer of Pacific salmon in lake sediments, it was also included. In total, 10 cores were used to relate down-core profiles of several different contaminants and δ^{15}N against historical counts of escapement. Significant relationships (after allowance of a certain delay between the curves) could be found in only one core for escapement and PCBs, and in 2 cores for escapement and δ^{15}N. A total of 3 cores were found to have significant relationships between δ^{15}N and contaminants. Usually, ΣPCBs achieved the best relationships, possibly because the probability that past and present contaminant patterns in salmon are being recorded by the ~100 congeners is relatively high.

Nevertheless, it became apparent that several factors have to be considered which might have a distorting influence on down-core profiles of the contaminants. The higher atmospheric input of POPs during the 1960's and 1970's often result in higher contaminant concentrations in the sediments, which are not related to salmon abundance. Elevated contaminant inputs can also be observed due to events in the watershed, or anthropogenic point sources. A very common feature in all lakes is a rise in contaminant concentrations toward the surface sediments, which can generally not be linked to sockeye salmon abundance. A recent study of a lake in the Canadian Arctic observed maximum concentrations of PCBs, endosulfan and other POPs at or near the sediment surface, corresponding to the findings presented here [143]. The authors hypothesized that climate change causes an enhanced algal productivity, which then leads to an increase in scavenging of contaminants from the water column [143]. In this study, algal productivity was not investigated, but it is conceivable that similar mechanisms play a role in these sub-Arctic lakes, which also experience a prolonged winter with extensive ice cover. Some indicators of lake productivity in the sediments, such as percent carbon, nitrogen, and organic matter, are increasing in almost all of the lakes. Usually it would be expected that such increases of productivity are accompanied by increases in δ^{13}C, since higher productivity would lead to more fractionation of the carbon isotopes [133]. However, it can also be expected that recent increases in atmospheric CO_2, which have lowered the atmospheric δ^{13}C [119], have an impact on the lake ecosystems. A study by Schelske and Hodell [133] looked at δ^{13}C in Lake Ontario sediments and found that values started to decline in 1977. They stated that the extensive fossil fuel burning in this century could be one of the causes.

Other difficulties in relating spawner abundance to sedimentary down-core profiles arise from the often very poor resolution, and the limited number of values that could be obtained from the sediment core — a problem that was usually related to cores with very low sedimentation rates. It should also be considered that elevated POP concentrations cannot be expected to start their appearance in sediment cores before the last 70 years or so, which is a very short time frame for a paleolimnological study.

It is very interesting to note that δ^{15}N, which was found to be a reliable indicator of sockeye salmon spawner abundance in several studies (e.g., [134, 56, 43, 44]), could only be clearly related to historical escapement numbers in 2 out of the 10 sediment cores. In Red Lake, denitrification was discussed as a possible reason for the almost negative relationship between past salmon spawner numbers and δ^{15}N values, although this scenario is usually unlikely for the mostly oligotrophic salmon nursery lakes, as mentioned earlier.

Another problem is the translation of sockeye spawner numbers to the salmon signal which is finally recorded in the sediments. Especially if spawner abundance is very variable (as seen with some lakes in B.C.), extracting the trend that could be expected in the sediments can be difficult. The fact that 3 of the B.C. lakes showed significant relationships between down-core profiles of δ^{15}N and contaminants, although in 2 of the lakes escapement could be neither related to δ^{15}N, nor to contaminants, indicates that the salmon signal in the sediments differed from averaged escapement numbers.

Overall, this study was able to show that although it is in principle possible to relate past sockeye spawner abundance to contaminant patterns in down-core profiles, several factors have to be considered which can distort the salmon signal. More studies are necessary to clarify the processes which influence the integration of salmon derived nutrients and contaminants into lake systems, in order to clearly establish the relationship between past salmon spawner abundance and salmon-derived contaminants in lake sediments.

Chapter 6

Discussion

The results presented in this thesis clearly show that there is a relationship between abundance of sockeye salmon spawners and contaminant concentrations in sediments of nursery lakes in B.C. and Alaska. The surface sediment analysis of 10 lakes revealed that higher sockeye salmon escapement was associated with higher contaminant concentrations in the sediments of those lakes. Overall, the highest spawner receiving lake had roughly 20 times the amount of ΣPCBs compared to the control lakes which did not receive any salmon. Although it appears that PCB concentrations in the sediments are directly proportional to the number of sockeye salmon spawners, the simple calculation:

spawner abundance $*$ PCB concentration in spawners $=$ PCB concentration in sediments

is not feasible due to the far more complex contaminant dynamics within the lakes. More precisely, if the theoretical calculation would be conducted for Red Lake, approximately 174.6 ng ΣPCBs m^{-2} yr^{-1} would have been brought in by salmon spawners (see Appendix for the detailed calculation). This can be compared to a focus corrected value of 635.6 ng ΣPCBs m^{-2} yr^{-1} that was measured in Red Lake sediments. Even if that value is subtracted with a possible atmospheric input of 125.7 ng ΣPCBs m^{-2} yr^{-1} (based on the focus corrected value of Kinaskan Lake, which only received contaminants by atmospheric deposition), the resulting value would still be ~3 times higher compared to the value that is calculated based on the ΣPCBs content of salmon samples. Moreover, contaminant losses due to volatilization, outflow and export by outgoing salmon smolts have to be included in the calculation, which would further increase the discrepancy between estimated salmon contaminant input and measured contaminant concentration in the sediments.

One explanation for the difference could of course be that salmon carried a higher load of contaminants in the past. Since historical measurements of contaminant concentrations are missing, it is difficult to determine if salmon had higher PCB concentrations in previous years. Nevertheless, if our own measurements are compared to those in the literature, it becomes apparent that more recent values are on average lower. For example, Easton et al. [37] measured an average of 5.4 ng ΣPCBs g^{-1} wet weight in B.C. sockeye salmon (n=2), Hites et al. [66] found an average of 7.2 ng ΣPCBs g^{-1} wet weight in B.C. sockeye salmon (n=3) and 3.41 ng ΣPCBs g^{-1} wet weight in sockeye from Kodiak from Alaska (n=3). Our own average for 23 sockeye salmon (20 from Kodiak Island and 3 from B.C.) is 6 ng ΣPCBs g^{-1} wet weight. All those salmon samples were measured between 2000 and 2004. In comparison, Ewald et al. [41] measured values of ~50 ng ΣPCBs g^{-1} wet weight in 1994 (values on a wet weight basis were calculated based on the given lipid concentration and seem to be the average of 20 sockeye salmon from Copper River, Alaska). It is therefore possible that contaminant concentrations in sockeye salmon did in fact change over time.

Lake internal processes related to contaminant deposition and burial in the sediments could also be responsible for a certain discrepancy between calculated and measured contaminant concentrations in the sediments. A recent study that tried to model contaminant concentrations of Arctic lakes which receive atmospheric deposition only, found that modeled water concentrations fell within the range of measured values [31]. Modeled sediment concentrations on the other hand had discrepancies to the measured concentrations of an order-of-magnitude or more, whereby the modeled concentrations were consistently lower [31]. Helm et al. [64] found large differences between modeled and measured sediment concentrations, as well, and argued that the discrepancies might be due to differences in the response times of water and sediments to temporal changes in loadings. They also noted the difficulty to infer the sediment loading of a lake based on one sample, since sediments are a heterogeneous medium [64]. This is supported by Oliver et al. [117], who looked at the distribution of contaminants in Lake Ontario sediments. Their study revealed that samples collected outside of sediment basins had 25 times lower contaminant concentrations compared to concentrations within the basins, and the authors highlighted the importance of sediment redistribution within the lake.

Another consideration for discrepancies between measured and expected contaminant loadings is the highly efficient transport mechanism of contaminants by salmon. Blais et al. (submitted) modeled the fugacities (the tendency of a chemical to escape) of the different media of a lake after a contaminant input by salmon. They concluded that although salmon deliver a relatively small fraction of chemicals, it is more efficient compared to inputs by water or air due the very direct delivery. Moreover, Blais et al. determined that because of the persistence of the pollutants, there is an considerable amount of 'carry over' from one year to the next, and that it takes at least 5 years for the abiotic fugacities to stabilize even after salmon are removed as a transport mechanism.

An additional modeling approach is theoretically given by the linear relationship between salmon spawners and ΣPCB concentration in surface sediments from 2002/03 in this study, which could be used to infer a 'proportionality constant'. This proportionality constant can be derived using the slope of the relationship and depicts the factor by which a ΣPCB concentration in lake sediments could be expected to rise if a certain number of salmon spawners contributes to the overall contaminant input to the lake. However, as evident from the down-core profiles, it has to be expected that other factors contribute to the relationship between spawner abundance and contaminant concentration, and these factors might change with time. Even though successful regressions between spawner abundance and ΣPCB down-core concentrations were done for Meziadin Lake, the same relationship could not be determined in the other lakes. This was often due to significant contaminant input by sources other than salmon, but the relationship is further complicated by the apparent changes of overall contaminant concentration, as well as contaminant composition in the salmon. It was already discussed above that contaminant concentrations in salmon probably declined over the last 10 years. Change in atmospheric contaminant concentration in the Canadian Arctic was also found in a recent study by Hung et al. [73]. The authors reported that several PCB congeners show declining trends in the atmosphere, some of which were accelerating in recent years, among them congeners that were abundant in salmon samples in this study (e.g. 101 and 138).

An even more influential factor might be that of climate warming, which has been reported to cause increases in contaminant deposition in lake sediments in previous studies [143, 101]. The same mechanism also might be responsible for the recent rise of contaminant flux to the sediments of the lakes investigated in this study, as seen in contaminant down-core profiles of almost all the lakes. A further increase in lake productivity, accompanied by changes in atmospheric contaminant deposition and differences in contaminant concentrations in salmon would substantially change the composition of the interacting factors which determine the relationship between spawner abundance and contaminant concentration in the sediments found in this study. It is thus unlikely that a proportionality constant derived from this study would be useful in future modeling exercises.

More studies will be needed to evaluate the processes which influence the cycling and fate of salmon-derived contaminants in lakes and the implications on food webs to allow for a successful development of predictive models. These models could also be extended to predict possible risk factors for human and environmental health, and will have to incorporate greater consideration of factors such as climate change.

Apart from the effect of higher primary productivity in lakes, which may cause the above mentioned increases in net flux of contaminants to the sediments, consequences of climate change can be manifold [101]. For instance, it is likely that climate warming influences the migrating behaviour of animals, and it has already been reported that Pacific salmon entered rivers in the Arctic that are historically not salmon spawning grounds [9]. Climate warming might also alter food web structures in lakes, which can have vital consequences for apex consumers. For example, the addition of only one trophic level in the food web might multiply the DDT concentration by 6 [101].

The implications for human health are substantial, if it is considered that consumption advisories for fish are already widespread. Currently, all of the Laurentian Great Lakes have fish-consumption advisories for several POPs [14], and the Government of Ontario frequently releases a guide to eating Ontario sport fish which gives consumption advice based on measurements of known POPs such PCBs, DDT, dioxins, etc. The USEPA reported in 2004 that a total of 3,221 fish advisories were issued in Canada and the U.S., which warned residents about the potential health risks associated with eating contaminated fish from local waters (http://map1.epa.gov/).

Hites et al. [66] recently assessed the comparative health risk of consuming farmed and wild salmon using an approach determined by the USEPA. The authors based their assessment on contaminant concentrations of PCBs, toxaphene and dieldrin that were measured in the salmon muscle tissue. They found that even wild sockeye salmon from Alaska and B.C., which are among the least contaminated, should not be consumed more than twice a month [66]. This assessment gains even more relevance if it is considered that these contaminant concentrations delivered by sockeye salmon to their nursery lakes form the basis on which the food web in those lakes is built.

Finally, it should be mentioned that current consumption advisories and risk assessments are mostly based on the well-known and extensively studied 'legacy' POPs. However, Hites et al. [67] extended their above mentioned analysis to include the newly emerging POPs called polybrominated diphenyl ethers (PBDEs), and determined that those chemicals are also abundant in salmon. PBDEs are used as flame retardants and were found to be inducers of the hepatic cytochrome P450 enzymes, are endocrine disruptors and might be carcinogenic [67]. Nevertheless, risk-based thresholds have not yet been established by the leading regulatory or public health agencies [67]. Considering these results, it can currently only be speculated about the biotransport capabilities of the >58,000 chemicals listed on the USEPA's Chemical Substances Inventory for 1985, and their possible consequences for human and environmental health, which makes the need for future research apparent.

Appendix A

Methods

A.1 Quality Control

Table A.1: Recoveries (averages and standard deviations) in percent for standard PCBs 30 and 204 and standard OC pesticides 1,3,5-TBB, 1,2,4,5-TBB, δ-HCH and endrin ketone in the analyzed samples.

Samples	PCBs		OC pesticides			
	30	204	1,3,5-TBB	1,2,4,5-TBB	δ-HCH	Endrin Ketone
Salmon	64 ± 8	74 ± 8	51 ± 11	51 ± 11	45 ± 5	81 ± 28
Surf. Seds.	77 ± 12	89 ± 32	29 ± 23	33 ± 23	34 ± 22	44 ± 37
B.C. Lakes						
Bowron	50 ± 10	60 ± 11	47 ± 8	53 ± 7	25 ± 4	43 ± 9
Fraser C-1	60 ± 6	89 ± 5	41 ± 18	40 ± 5	38 ± 4	47 ± 11
Kinaskan	65 ± 10	82 ± 9	45 ± 13	39 ± 10	34 ± 4	39 ± 8
Meziadin	57 ± 5	69 ± 4	53 ± 7	53 ± 8	44 ± 14	55 ± 20
Quesnel	52 ± 5	63 ± 4	63 ± 16	57 ± 13	17 ± 8	26 ± 11
Shuswap	74 ± 11	90 ± 18	56 ± 10	48 ± 10	59 ± 5	72 ± 12
Alaskan Lakes						
Frazer	29 ± 9	41 ± 11	48 ± 14	41 ± 8	44 ± 12	42 ± 21
Karluk	33 ± 5	43 ± 7	37 ± 5	32 ± 4	36 ± 4	35 ± 8
Red	38 ± 7	42 ± 7	34 ± 6	32 ± 6	46 ± 3	46 ± 4
Upper Olga	91 ± 80	73 ± 31	51 ± 34	55 ± 46	69 ± 36	93 ± 46

Table A.2: RD recoveries (averages and standard deviations) in percent for PCB congeners in the sediment analysis. Data is based on 9 RDs.

PCB	Average ± Stdev.	PCB	Average ± Stdev.	PCB	Average ± Stdev.
1	71 ± 38	63	91 ± 29	129	92 ± 26
3	109 ± 54	74	100 ± 31	178	108 ± 35
4-10	74 ± 38	70-76-98	97 ± 32	175	96 ± 27
7-9	87 ± 36	66-95	111 ± 63	187-182	99 ± 28
6	109 ± 35	91-55	96 ± 33	183	92 ± 26
8-5	74 ± 35	56-60	87 ± 31	128	98 ± 29
19	96 ± 31	92	101 ± 28	167	103 ± 29
30 (std)	75 ± 26	84	109 ± 33	185	96 ± 26
12-13	102 ± 43	101	119 ± 35	174	96 ± 25
18	95 ± 36	99	104 ± 28	177	97 ± 32
15-17	96 ± 33	119	97 ± 30	202-171-156	90 ± 29
24-27	81 ± 34	83	143 ± 135	173	87 ± 23
16-32	86 ± 33	97	108 ± 30	157-200	89 ± 28
54-29	91 ± 33	87-81	99 ± 31	204 (std)	87 ± 21
26	94 ± 35	136	86 ± 37	172	88 ± 25
25	214 ± 138	110	110 ± 33	197	92 ± 26
50-31-28	108 ± 60	82	95 ± 32	180	95 ± 27
33-20-53	109 ± 71	151	100 ± 30	193	98 ± 26
51	109 ± 35	135-144	93 ± 31	191	100 ± 31
22	94 ± 31	149	105 ± 31	199	96 ± 31
45	99 ± 34	118	112 ± 34	170-190	95 ± 29
46	98 ± 34	133	101 ± 29	198	92 ± 27
52	110 ± 36	146	97 ± 29	201	94 ± 26
49	105 ± 39	153-132-105	101 ± 36	203-196	92 ± 27
48-47	84 ± 28	141-179	93 ± 29	189	87 ± 27
44	101 ± 32	137	89 ± 30	207	92 ± 30
59-42	76 ± 29	176-130	45 ± 11	194	90 ± 27
40	91 ± 33	138-163	107 ± 34	205	102 ± 31
100	98 ± 32	158	91 ± 26	209	93 ± 24

Table A.3: RD recoveries (averages and standard deviations) in percent for OC pesticides in the sediment analysis. Data is based on 10 RDs.

Compound	Average ± Stdev.
PECB	37 ± 15
a-HCH	53 ± 29
HCB	43 ± 17
1,2,4,5-TTBB	40 ± 21
g-HCH	55 ± 30
d-HCH	48 ± 32
Heptachlor	59 ± 32
Aldrin	51 ± 21
Heptachlor Epoxide	54 ± 31
g-Chlordane	66 ± 32
a-Endosulfan	61 ± 36
a-Chlordane	66 ± 29
Dieldrin	64 ± 31
p,p'-DDE	71 ± 26
Endrin	63 ± 46
b-Endosulfan	32 ± 17
p,p'-DDD	68 ± 37
o,p'-DDT	73 ± 48
p,p'-DDT	42 ± 32
Endrin Ketone	61 ± 51
Methoxychlor	69 ± 44

Table A.4: Method detection limits for the OC pesticides. Data is in pg g^{-1} dry weight for sediments, and pg g^{-1} wet weight for salmon.

Compound	Surface Sediments (n=6)	Alaska 2002[a] (n=4)	B.C.[1][b] (n=3)	B.C.[2][c] (n=3)	Salmon (n=7)
PECB	26.52	32.03	18.19	2.34	3.95
α-HCH	114.60	112.91	17.70	0.00	6.36
HCB	23.88	29.36	20.17	1.82	30.66
γ-HCH	78.80	80.98	7.86	12.61	6.34
Heptachlor	24.79	30.55	1.34	1.15	0.00
Aldrin	27.52	34.18	9.32	3.49	0.00
Heptachlor Epoxide	0.00	0.00	0.00	0.00	0.00
γ-Chlordane	230.57	170.48	68.76	4.56	6.24
α-Endosulfan	6.25	7.57	0.00	8.29	0.00
α-Chlordane	144.79	107.56	34.61	16.48	4.92
Dieldrin	31.41	37.79	0.00	0.00	0.00
p,p'-DDE	300.97	192.58	90.47	1.87	3.83
Endrin	54.00	67.17	4.76	23.09	10.34
β-Endosulfan	2.86	0.00	0.00	4.05	12.22
p,p'-DDD	13.16	16.12	8.62	0.00	0.00
o,p'-DDT	99.51	82.48	46.48	3.21	0.00
p,p'-DDT	209.82	198.46	27.00	6.13	0.00
Methoxychlor	154.00	160.83	92.04	142.16	96.42

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[a] Includes Frazer, Karluk, Red, Spiridon and Upper Olga.

[b] Includes Quesnel, Bowron and Shuswap.

[c] Includes Meziadin, Kinaskan and Fraser.

Table A.5: Method detection limits of PCB congeners for the surface sediments (data is in pg g^{-1} dry weight and is based on 3 method blanks).

PCB	Amount	PCB	Amount	PCB	Amount
1	0.00	74	33.68	178	16.80
3	0.00	70-76-98	39.32	175	0.00
4-10	0.00	91-55	20.55	187-182	179.88
7-9	0.00	56-60	4.16	183	27.84
6	0.00	92	39.31	128	42.14
8-5	86.41	84	19.52	167	20.27
19	0.00	101	152.43	185	2.00
12-13	0.00	99	59.46	174	14.43
18	23.84	119	0.00	177	35.96
15-17	114.63	83	12.26	202-171-156	56.03
24-27	0.00	97	78.52	173	0.00
16-32	22.73	87-81	40.77	157-200	0.00
54-29	0.00	136	20.70	172	0.00
26	29.74	110	114.75	197	0.00
25	0.00	82	14.06	180	39.73
50-31-28	86.94	151	29.20	193	0.00
33-20-53	10.12	135-144	45.49	191	20.99
51	0.00	147-107	18.25	199	16.50
22	3.70	149	108.41	170-190	38.93
45	25.78	118	151.53	198	31.82
46	0.00	133	148.81	201	63.76
52	4.25	146	62.74	203-196	54.12
49	0.00	153-132-105	189.26	189	0.00
48-47	89.89	141-179	75.19	208-195	31.09
44	21.24	137	14.79	207	17.56
59-42	25.54	176-130	13.03	194	63.11
40	16.94	138-163	115.35	205	0.00
100	18.02	158	30.55	206	42.95
63	0.00	129	12.83	209	0.00
				sum	3060.55

Table A.6: Method detection limits of PCB congeners for the Alaska down-core sediments (data is in pg g^{-1} dry weight and is based on 4 method blanks).

PCB	Amount	PCB	Amount	PCB	Amount
1	0.00	74	24.73	129	12.53
3	587.74	70-76-98	56.42	178	20.71
4-10	0.00	91-55	13.83	175	0.00
7-9	48.34	56-60	14.53	187-182	72.78
6	66.21	92	14.66	183	33.54
8-5	138.11	84	109.86	128	52.47
19	0.00	101	105.29	167	11.38
12-13	0.00	99	50.18	185	22.97
18	84.38	119	0.00	174	38.42
15-17	101.99	83	149.32	177	12.29
24-27	12.47	97	43.79	202-171-156	81.23
16-32	60.48	87-81	63.05	173	0.00
54-29	0.00	136	5.76	157-200	2.85
26	0.00	110	113.62	172	7.20
25	0.00	82	50.10	197	0.00
50-31-28	119.05	151	28.18	180	162.78
33-20-53	83.89	135-144	23.78	193	71.11
51	0.00	147-107	29.78	191	0.00
22	46.02	149	102.53	199	20.96
45	27.18	118	116.96	170-190	33.06
46	0.00	133	18.35	198	4.75
52	91.22	146	10.75	201	64.09
49	0.00	153	104.20	203-196	61.72
48-47	47.22	132-105	92.64	189	0.00
44	45.08	141-179	44.28	208-195	11.36
59-42	20.86	137	3.13	207	14.70
40	10.91	176	9.83	194	36.02
100	0.00	138-163	127.36	205	0.00
63	0.00	158	19.50	206	39.03
				209	0.00
				sum	4025.52

Table A.7: Method detection limits of PCB congeners for Quesnel, Bowron and Shuswap lakes (data is in pg g^{-1} dry weight) and is based on 3 method blanks.

PCB	Amount	PCB	Amount	PCB	Amount
1	68.63	74	13.12	178	3.61
3	0.00	70-76-98	56.45	175	0.00
4-10	24.29	91-55	21.03	187-182	47.13
7-9	16.06	56-60	15.56	183	14.23
6	23.11	92	19.37	128	21.52
8-5	45.67	84	42.32	167	2.93
19	4.98	101	88.13	185	0.00
12-13	0.00	99	37.08	174	12.83
18	29.35	119	0.00	177	20.67
15-17	28.53	83	35.46	202-171-156	27.69
24-27	3.63	97	64.41	173	0.00
16-32	21.20	87-81	77.32	157-200	1.44
54-29	6.53	136	17.45	172	2.32
26	12.91	110	100.72	197	0.00
25	0.00	82	11.46	180	17.02
31-28	94.83	151	11.67	193	0.00
33-20-53	31.19	135-144	19.37	191	2.16
51	0.00	147-107	5.72	199	0.00
22	15.50	149	59.83	170-190	5.14
45	5.45	118	82.47	198	0.00
46	3.20	133	5.23	201	6.39
52	68.34	146	8.50	203-196	4.69
49	0.00	"153,132-105"	102.65	189	0.00
48-47	14.89	141-179	25.73	208-195	3.28
44	45.89	137	15.18	207	5.14
59-42	0.67	176-130	4.65	194	6.07
40	6.40	138-163	84.81	205	0.00
100	0.00	158	9.47	206	0.00
63	0.00	129	7.35	209	4.86
				sum	1822.88

Table A.8: Method detection limits of PCB congeners for Meziadin, Kinaskan and Fraser lakes (data is in pg g^{-1} dry weight) and is based on 3 method blanks.

PCB	Amount	PCB	Amount	PCB	Amount
1	0.00	74	3.55	178	3.02
3	0.00	70-76-98	1.95	175	6.24
4-10	8.87	91-55	2.35	187-182	3.76
7-9	0.00	56-60	7.37	183	0.92
6	0.00	92	2.40	128	3.56
8-5	0.00	84	3.06	167	0.00
19	0.00	101	4.71	185	0.00
12-13	0.00	99	2.80	174	1.83
18	7.14	119	0.00	177	8.74
15-17	12.28	83	3.21	202-171-156	12.48
24-27	0.00	97	14.51	173	0.00
16-32	14.56	87-81	4.43	157-200	0.00
54-29	9.58	136	0.00	172	0.00
26	8.55	110	2.07	197	0.00
25	4.98	82	1.26	180	1.28
31-28	16.57	151	5.58	193	3.91
33-20-53	9.36	135-144	10.48	191	7.39
51	0.00	147-107	0.00	199	0.00
22	2.00	149	3.18	170-190	9.02
45	0.00	118	5.85	198	0.00
46	10.55	133	0.00	201	5.43
52	4.36	146	53.50	203-196	1.72
49	0.00	153-132-105	19.17	189	2.05
48-47	0.00	141-179	3.57	208-195	4.90
44	0.00	137	1.73	207	6.45
59-42	0.00	176-130	0.00	194	0.00
40	0.00	138-163	14.51	205	0.00
100	0.00	158	2.63	206	0.00
63	0.00	129	0.00	209	6.43
				sum	371.82

Table A.9: Method detection limits of PCB congeners for salmon samples (data is in pg g^{-1} wet weight and is based on 8 method blanks).

PCB	Amount	PCB	Amount	PCB	Amount
1	0.00	74	3.59	178	2.12
3	0.00	70-76-98	11.63	175	1.95
4-10	0.00	91-55	3.11	187-182	5.47
7-9	0.00	56-60	3.98	183	0.00
6	0.00	92	1.98	128	1.22
8-5	0.00	84	2.04	167	9.02
19	0.00	101	5.27	185	1.79
12-13	0.00	99	4.77	174	1.99
18	25.36	119	0.00	177	2.21
15-17	35.30	83	4.35	202-171-156	5.31
24-27	0.00	97	5.40	173	1.69
16-32	0.00	87-81	7.66	157-200	0.00
54-29	11.75	136	0.00	172	3.23
26	9.07	110	9.35	197	2.09
25	0.00	82	1.52	180	5.31
31-28	26.30	151	2.44	193	2.11
33-20-53	11.93	135-144	9.53	191	8.53
51	0.00	147-107	4.99	199	1.63
22	0.00	149	3.37	170-190	5.30
45	4.83	118	7.37	198	2.06
46	0.00	133	7.38	201	1.72
52	12.86	146	14.82	203-196	3.73
49	0.00	153-132-105	9.51	189	2.09
48-47	11.86	141-179	3.01	208-195	3.28
44	8.42	137	1.29	207	2.53
59-42	3.42	176-130	1.48	194	1.77
40	0.00	138-163	3.68	205	1.51
100	0.00	158	1.75	206	1.78
63	3.97	129	1.81	209	2.13
				sum	385.73

Table A.10: RF sediment values (averages and standard deviations) for the OC pesticides and the percentage reached in comparison to the certified value. Data is in ng g^{-1} dry weight and is based on 5 RFs.

Compound	Average	Stdev.	Percent of certified value
PECB	1.27	0.82	N/A[a]
α-HCH	0.07	0.17	N/A[a]
HCB	2.29	1.42	37.95
γ-HCH	0.99	0.65	N/A[a]
Heptachlor	0.63	1.12	N/A[a]
Aldrin	0.17	0.38	N/A[a]
Heptachlor Epoxide	8.54	8.26	N/A[a]
γ-Chlordane	7.69	7.84	N/A[a]
α-Endosulfan	10.50	11.65	N/A[a]
α-Chlordane	10.28	5.66	62.28
Dieldrin	3.26	3.88	N/A[a]
p,p'-DDE	47.03	18.05	54.69
Endrin	3.10	6.92	N/A[a]
β-Endosulfan	47.97	48.51	N/A[a]
p,p'-DDD	44.56	48.73	41.26
o,p'-DDT	14.79	14.02	N/A[a]
p,p'-DDT	105.38	56.76	88.56
Methoxychlor	14.72	5.94	N/A[a]

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[a] No data available.

Table A.11: RF sediment averages and standard deviations for PCB congeners. Data is in ng g^{-1} dry weight and is based on 5 RFs.

PCB	Average±Stdev.	PCB	Average±Stdev.	PCB	Average±Stdev.
1	0.38±0.39	74	14.77±4.19	178	2.02±0.48
3	3.99±3.94	70-76-98	38.20±10.95	175	0.72±0.47
4-10	1.67±1.09	91-55	3.36±3.23	187-182	10.79±2.56
7-9	1.63±0.33	56-60	19.28±4.92	183	4.96±1.08
6	3.46±0.33	92	7.03±2.07	128	4.45±1.10
5-8	6.73±3.96	84	5.27±3.32	167	1.62±0.43
19	2.18±0.58	101	29.00±7.63	185	1.03±0.28
12-13	0.00±0.00	99	12.28±3.55	174	7.65±1.88
18	23.58±5.90	119	1.33±0.45	177	4.45±1.06
15-17	22.87±5.10	83	1.74±0.69	202-171-156	6.14±2.26
24-27	2.30±0.40	97	9.34±2.46	173	0.12±0.13
16-32	15.99±3.69	87-81	17.79±5.19	157-200	1.74±0.34
54-29	0.49±0.70	136	0.00±0.00	172	1.55±0.23
26	11.78±1.95	110	30.74±8.31	197	0.12±0.15
25	4.34±1.04	82	3.93±1.11	180	17.58±4.31
31-28	75.09±19.69	151	6.08±1.66	193	0.87±0.25
33-20-53	23.03±5.97	135-144	5.75±1.59	191	0.36±0.23
51	1.60±0.95	147-107	3.10±1.59	199	0.73±0.14
22	12.20±2.93	149	22.57±6.86	170-190	8.65±1.71
45	5.61±1.51	118	23.57±6.82	198	0.42±0.22
46	2.37±0.67	133	1.94±0.47	201	4.85±1.06
52	37.40±10.90	146	4.90±1.14	203-196	5.31±1.00
49	0.00±0.00	153-132-105	46.53±15.49	189	0.49±0.17
48-47	16.20±4.11	141-179	9.52±2.01	208-195	3.01±0.54
44	27.11±7.77	137	1.69±0.66	207	0.63±0.25
59-42	8.24±5.03	176-130	0.38±0.52	194	4.17±0.77
40	6.07±1.07	138-163	28.76±7.75	205	0.48±0.09
100	1.63±0.43	158	2.71±0.86	206	3.42±0.59
63	1.68±0.60	129	1.32±0.30	209	2.95±0.58

Table A.12: The percentage reached of RF certified values for the PCB congeners where data was available.

PCB	Percent of RF value
18	46.24
52	47.10
44	45.04
101	39.50
99	32.75
87-81	59.49
110	48.41
151	35.91
149	45.41
118	40.64
138-163	46.31
187-182	43.01
183	40.65
128	52.52
180	39.68
170-190	38.26
194	37.20
206	37.10
209	43.25

Appendix B

Dating

Total ^{210}Pb profiles for all cores taken in 2001–2003 (Figure B.1) and 1995–1998 (Figure B.2). All ^{210}Pb were fitted using the equation

$$y = p_2 * e^{-xp_1} + p_3 * (1 - e^{-xp_1}).$$

p_3 equaled supported ^{210}Pb concentrations where background was reached. Background ^{210}Pb values were not reached and had to be inferred from ^{226}Ra concentrations for the following cores shown in Figure B.1: Frazer, Karluk, Red, and Upper Olga. The sedimentation rate was calculated by multiplying p_1 with λ (λ = ^{210}Pb constant, 0.0311 yr^{-1}); the inventory was obtained by multiplying p_1 with p_2. Values for sedimentation rates and ^{210}Pb inventories can be found in Table 3.1.

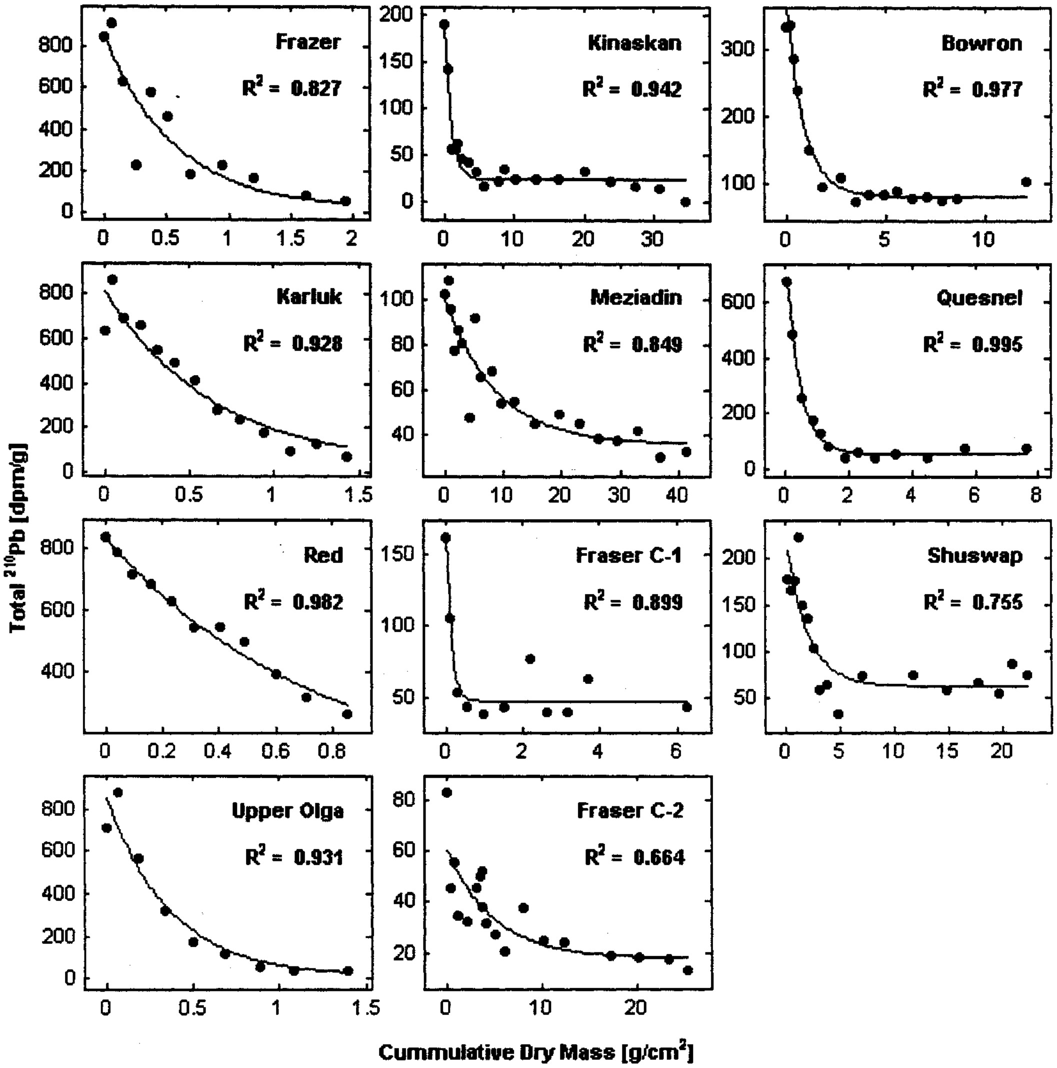


Figure B.1: Total ^{210}Pb profiles for cores taken in 2001–2003

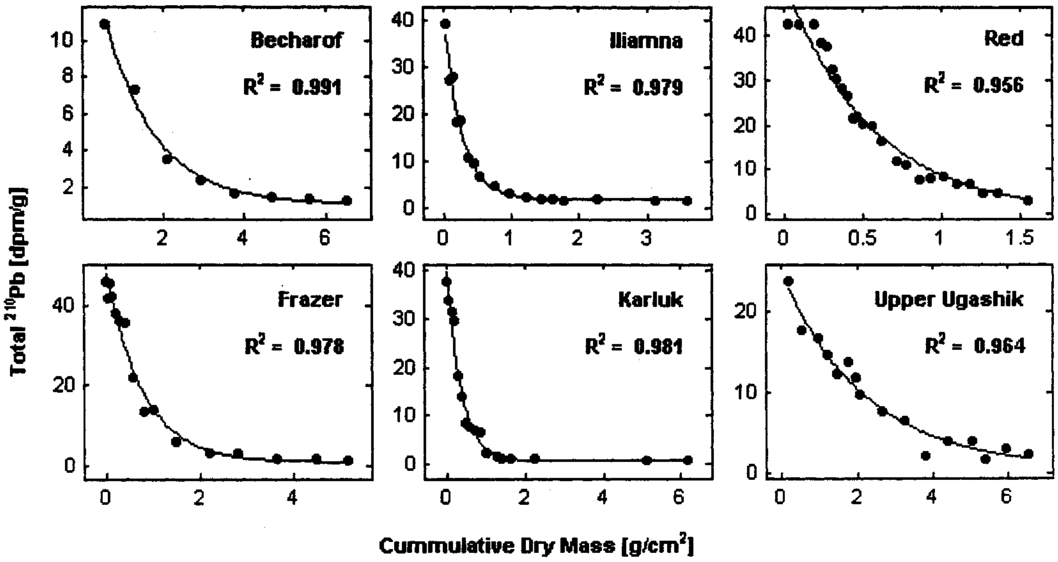


Figure B.2: Total ^{210}Pb profiles for cores taken in 1995–1998.

Figure B.3 shows plots of the radioisotopes ^{210}Pb, ^{226}Ra and ^{137}Cs for the lakes cored in 2001–2003. Total ^{210}Pb reaches background concentrations and equilibrium with ^{226}Ra in all cores except in those from lakes Frazer, Karluk and Red. In two cores (Bowron and Fraser C-1) ^{210}Pb background concentrations are reached, but ^{210}Pb is not in equilibrium with ^{226}Ra. A peak in ^{137}Cs is used as an independent marker of the year 1963, when fallout of ^{137}Cs was highest due to atomic weapons testing in North America.

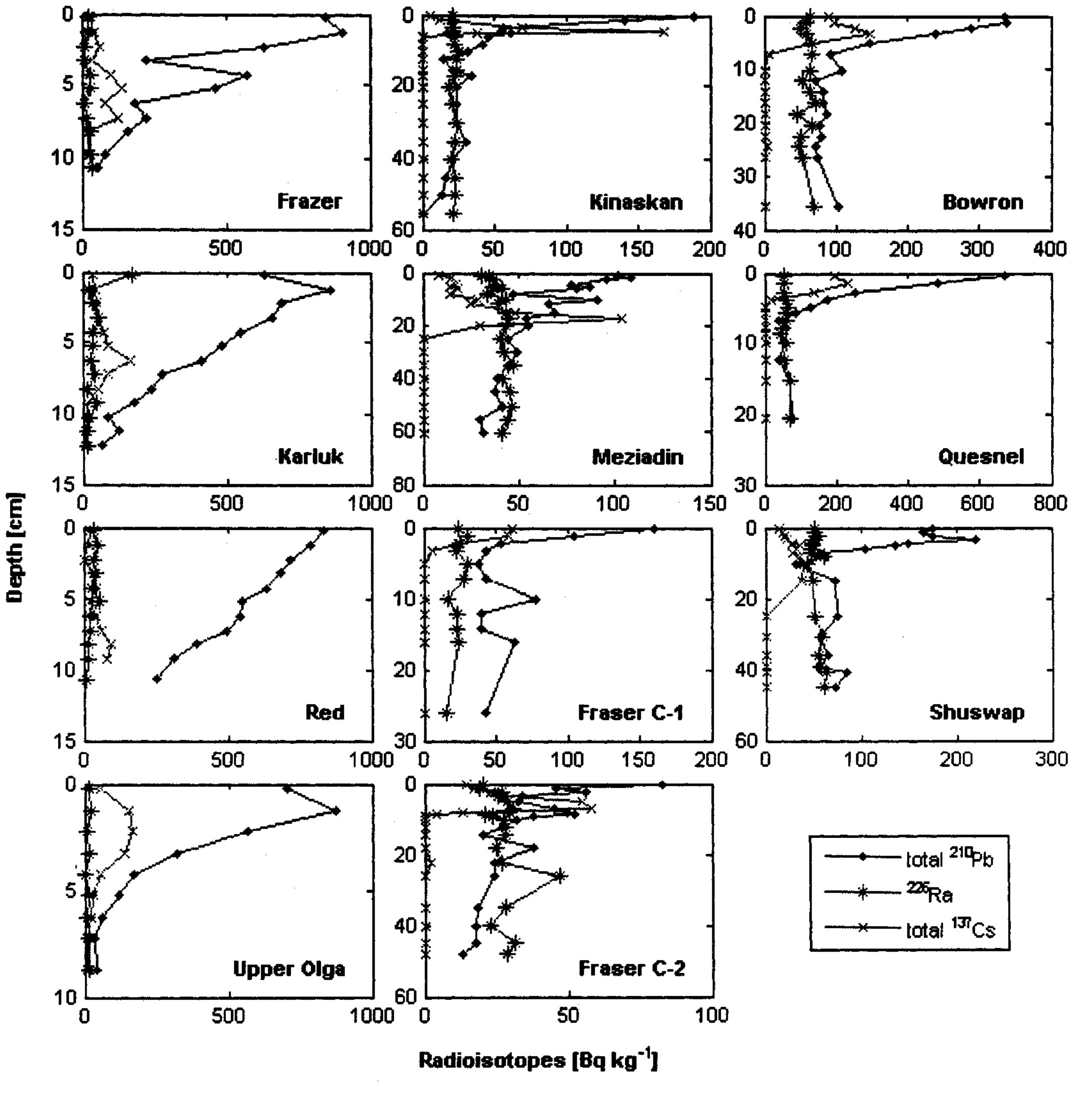


Figure B.3: Radioisotopes ^{210}Pb, ^{226}Ra and ^{137}Cs in the cores taken in 2001–2003.

Figures B.5 – B.4 show plots of the CFCS, CRS and CIC dating models for all of the lakes cored in 2001-2003. The depth of the ^{137}Cs peak is also plotted as an independent marker to allow for validation of the models. For clarity, error bars are plotted for CRS models for year (x-axis), and for the ^{137}Cs peaks for depth (y-axis) only.

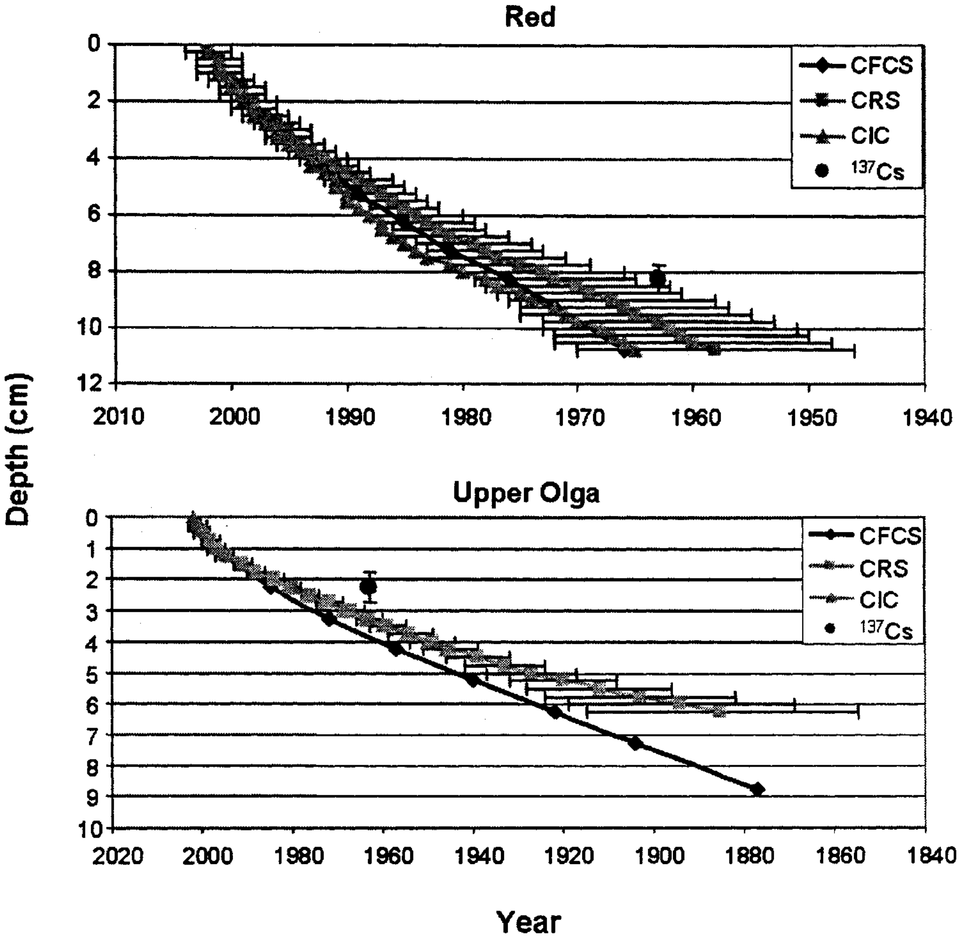
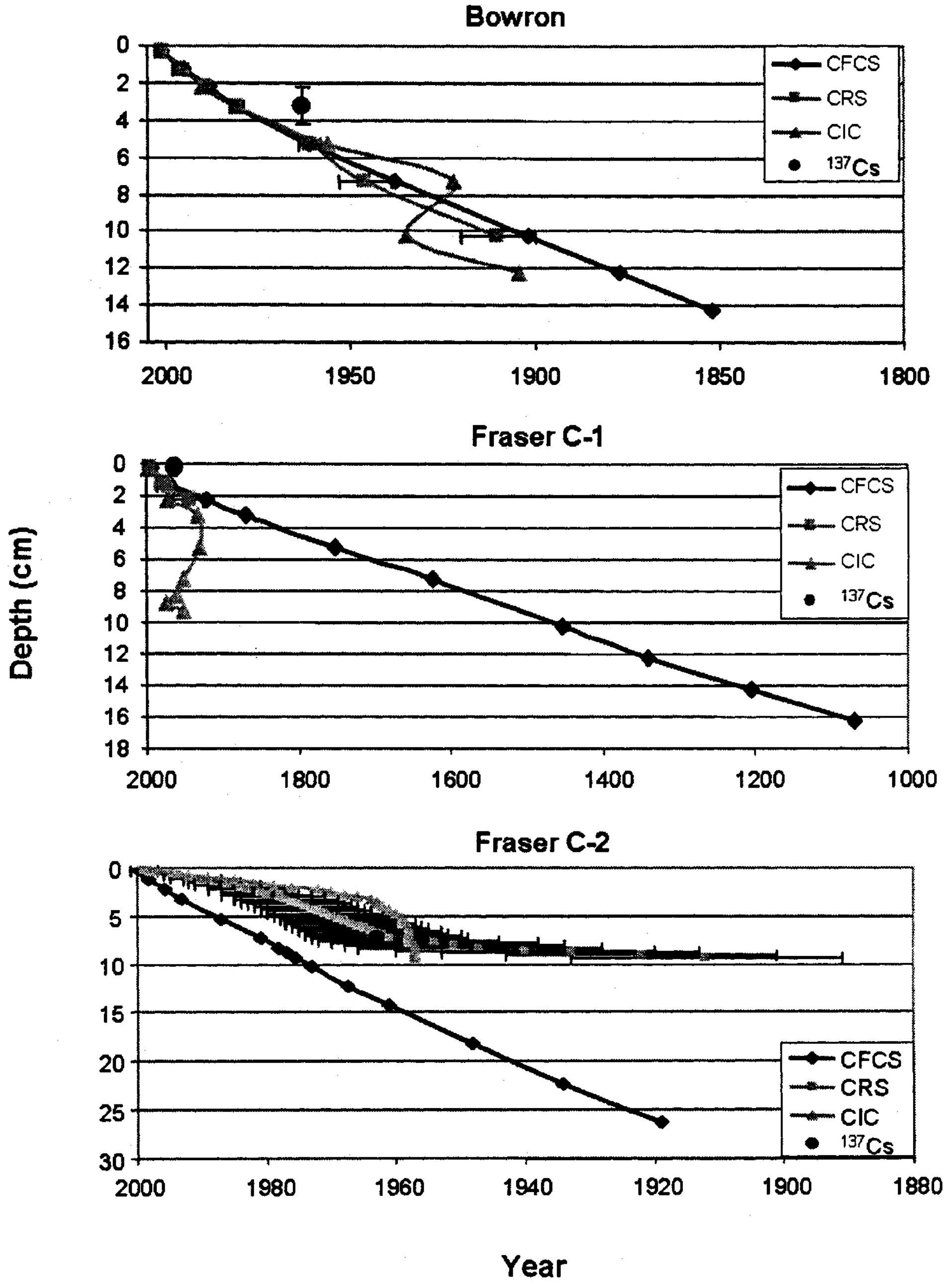


Figure B.4: Dating models for lakes cored in 2001–2003



Bowron

Fraser C-1

Fraser C-2

Figure B.5: Dating models for the lakes cored in 2001 – 2003

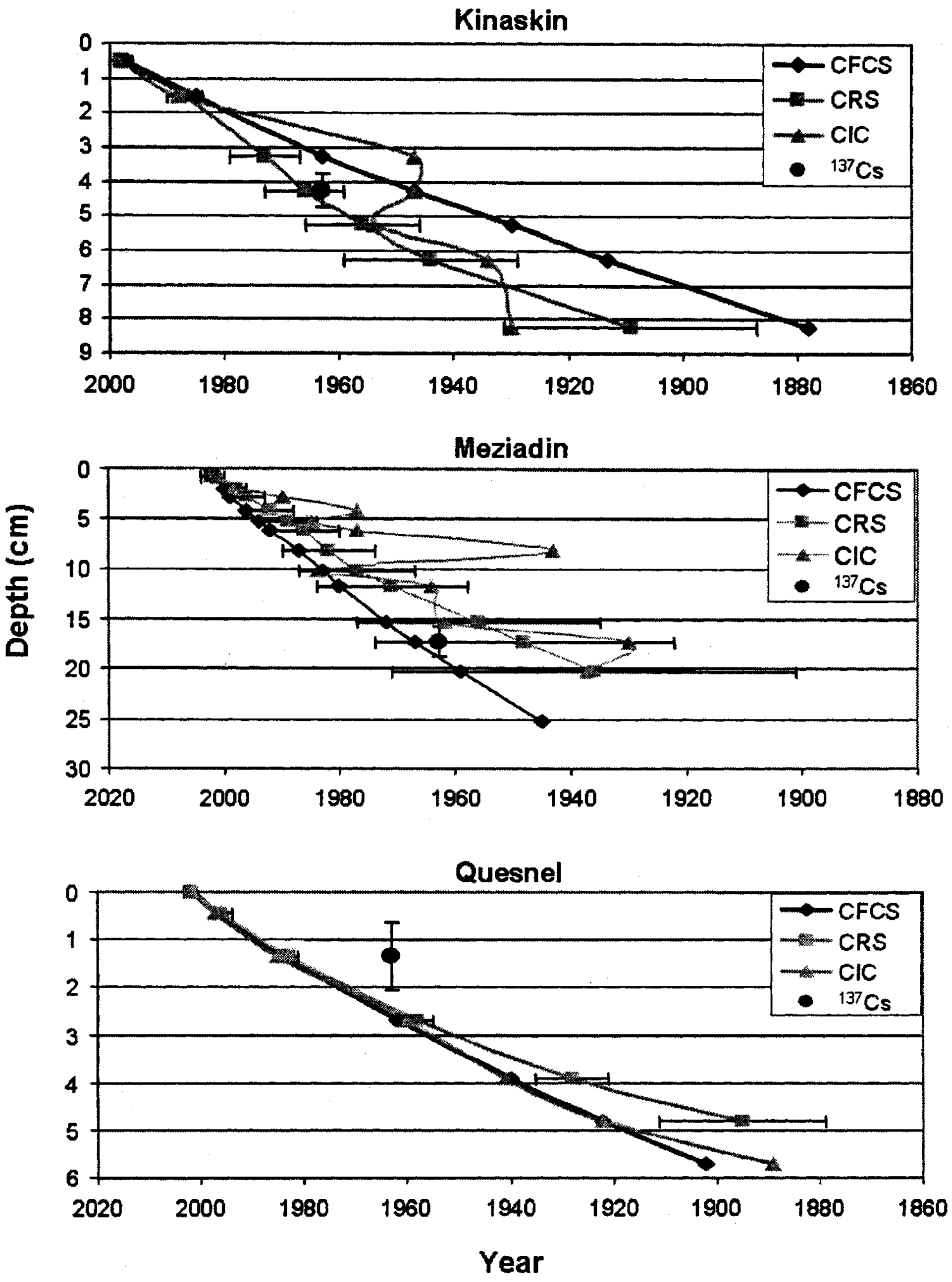


Figure B.6: Dating models for lakes cored in 2001 – 2003

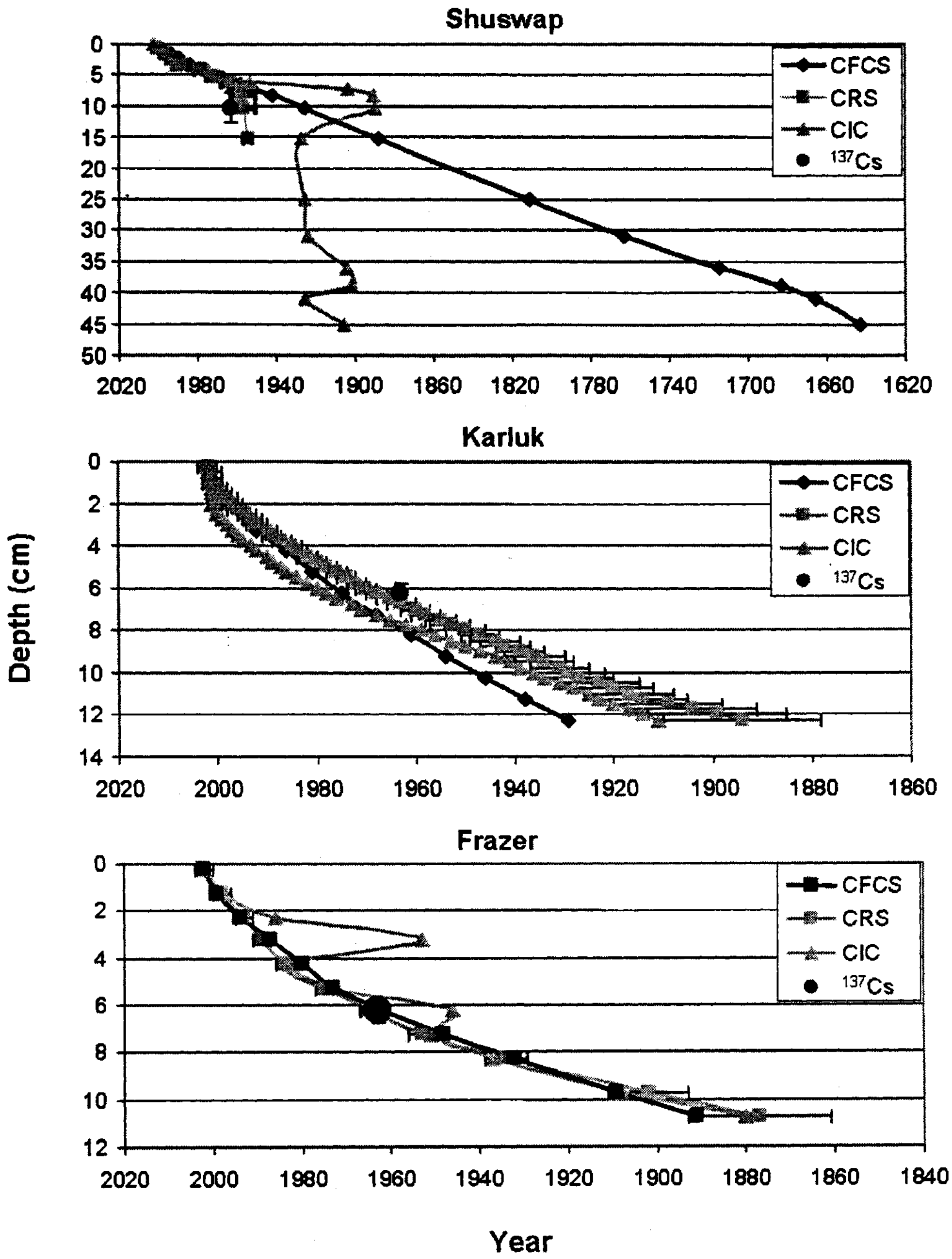


Figure B.7: Dating models for lakes cored in 2001 – 2003

Appendix C

Surface sediments

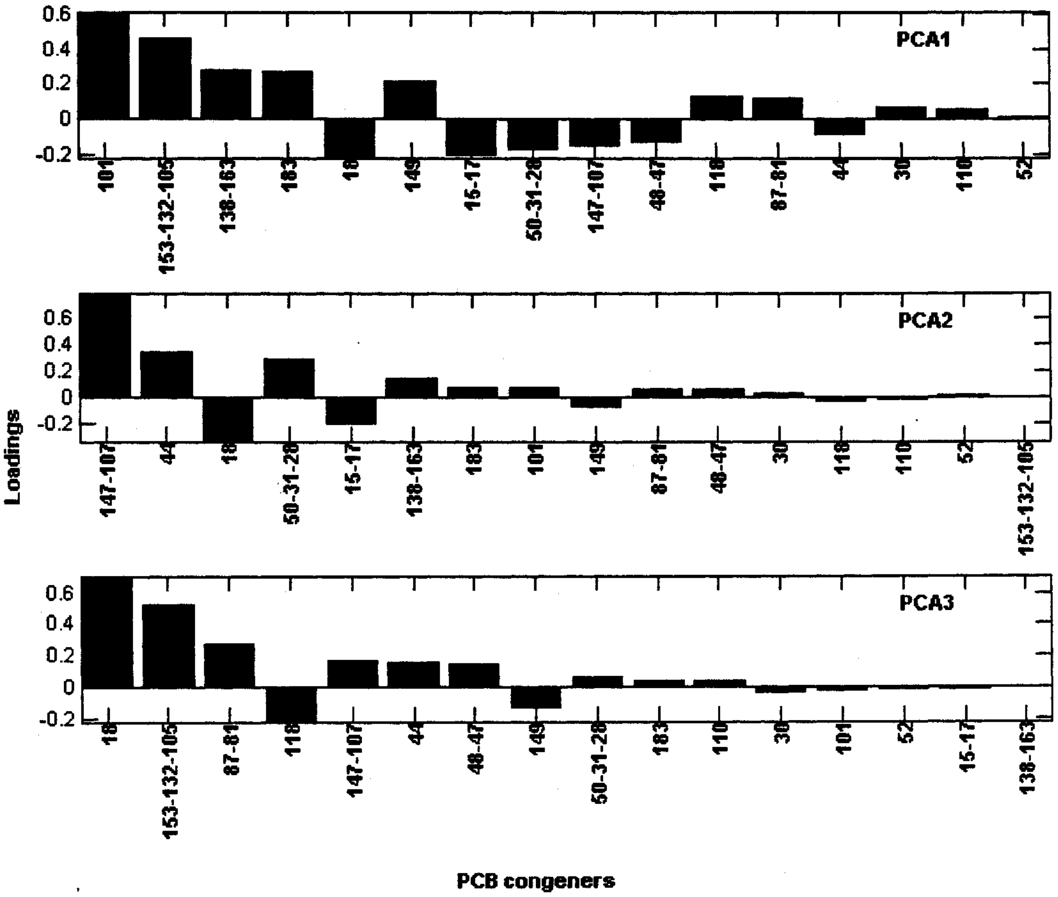


Figure C.1: Loadings of the 16 analytes for PCA1 (top), PCA2 (middle), and PCA3 (bottom).

Appendix D

Down-core profiles

D.1 Meziadin Lake

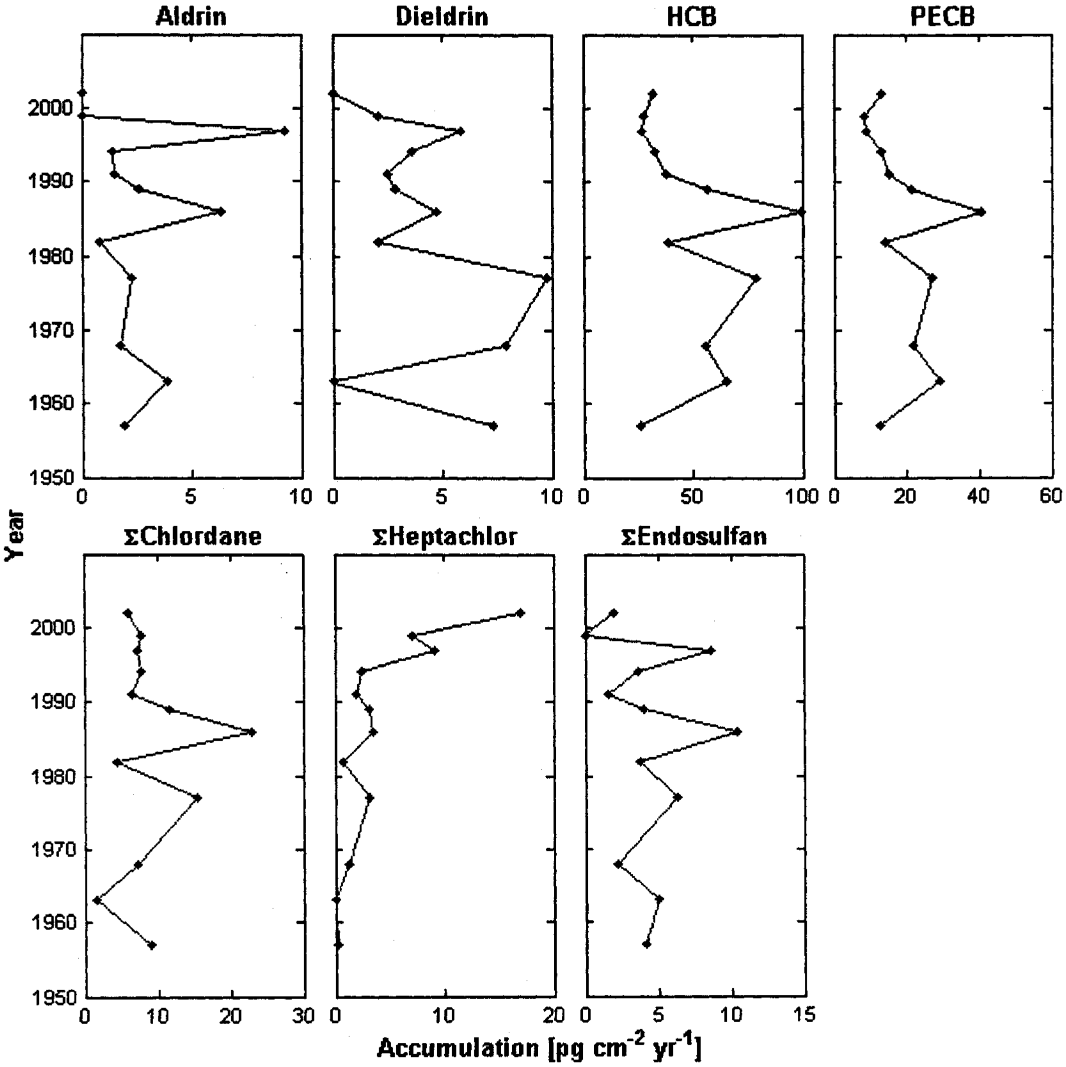


Figure D.1: Down-core profiles of individual OC pestidices Aldrin, Dieldrin, HCB and PECB, and sums of chlordane, heptachlor, and endosulfan fluxes in Meziadin Lake.

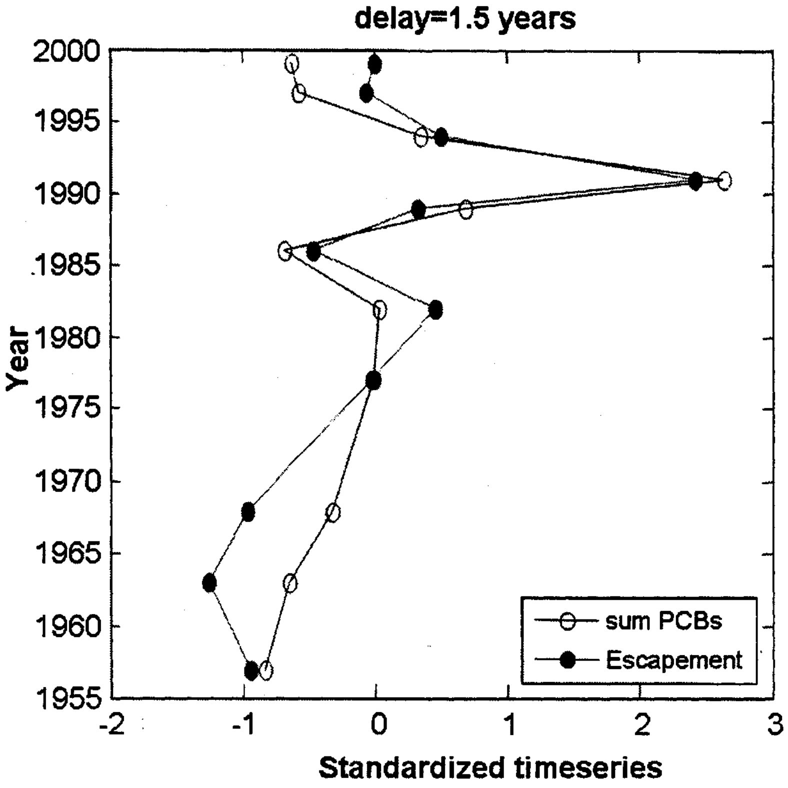


Figure D.2: The process of shifting time-series as explained in Chapter 5, shown here for the down-core profile of ΣPCB concentration and escapement in Meziadin Lake. The escapement curve was shifted downward and achieved the best fit after a delay of 1.5 years, which is within dating errors.

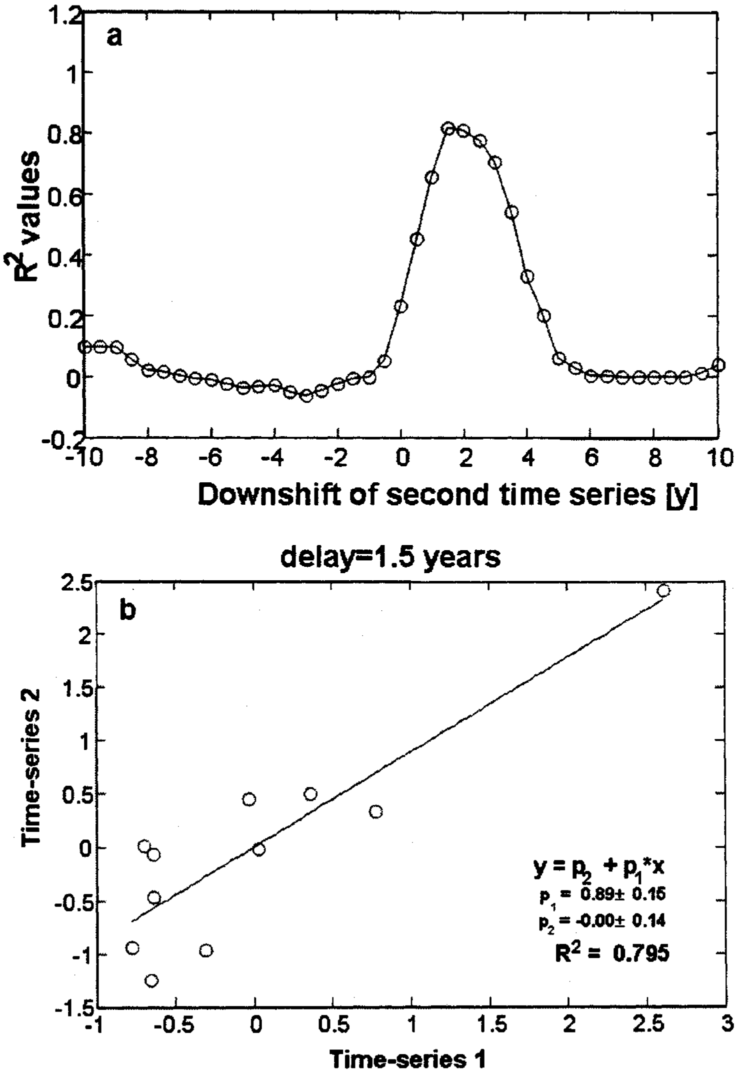


Figure D.3: a, the resulting changes in R^2 from the shifting process of the down-core profile of ΣPCBs against escapement; b, the correlation after a delay of 1.5 years.

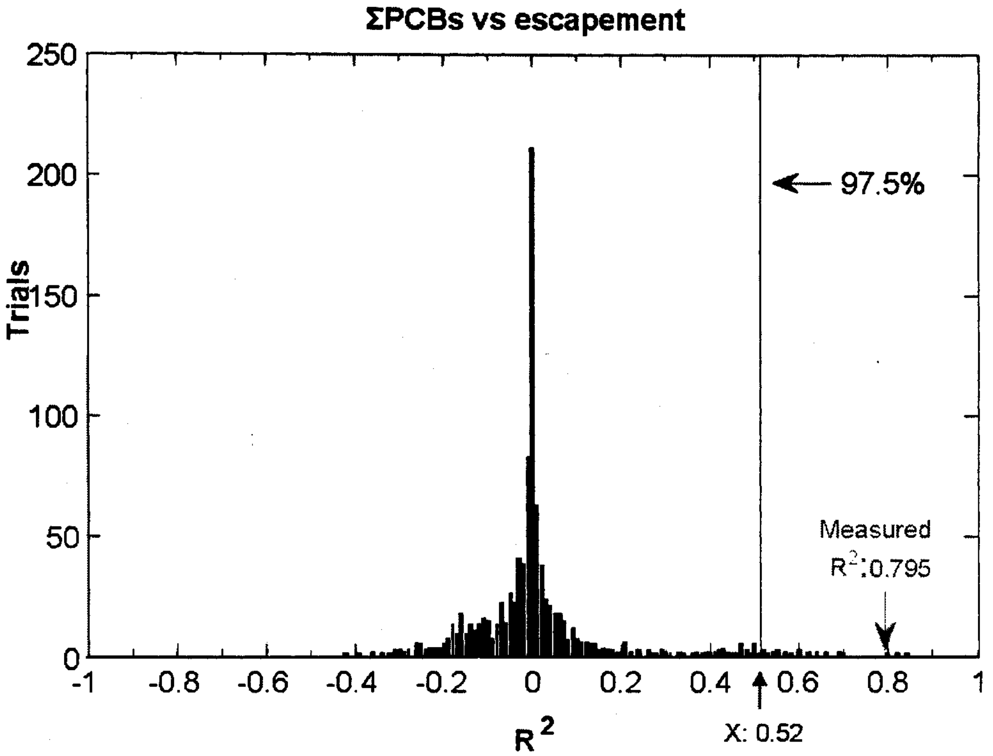


Figure D.4: The bootstrapping for ΣPCB concentration versus escapement. The vertical line indicates the level above which a significance of 97.5% is reached. The R^2 value at this level is specified below the line. The initially determined R^2 is also indicated.

D.2 Shuswap Lake

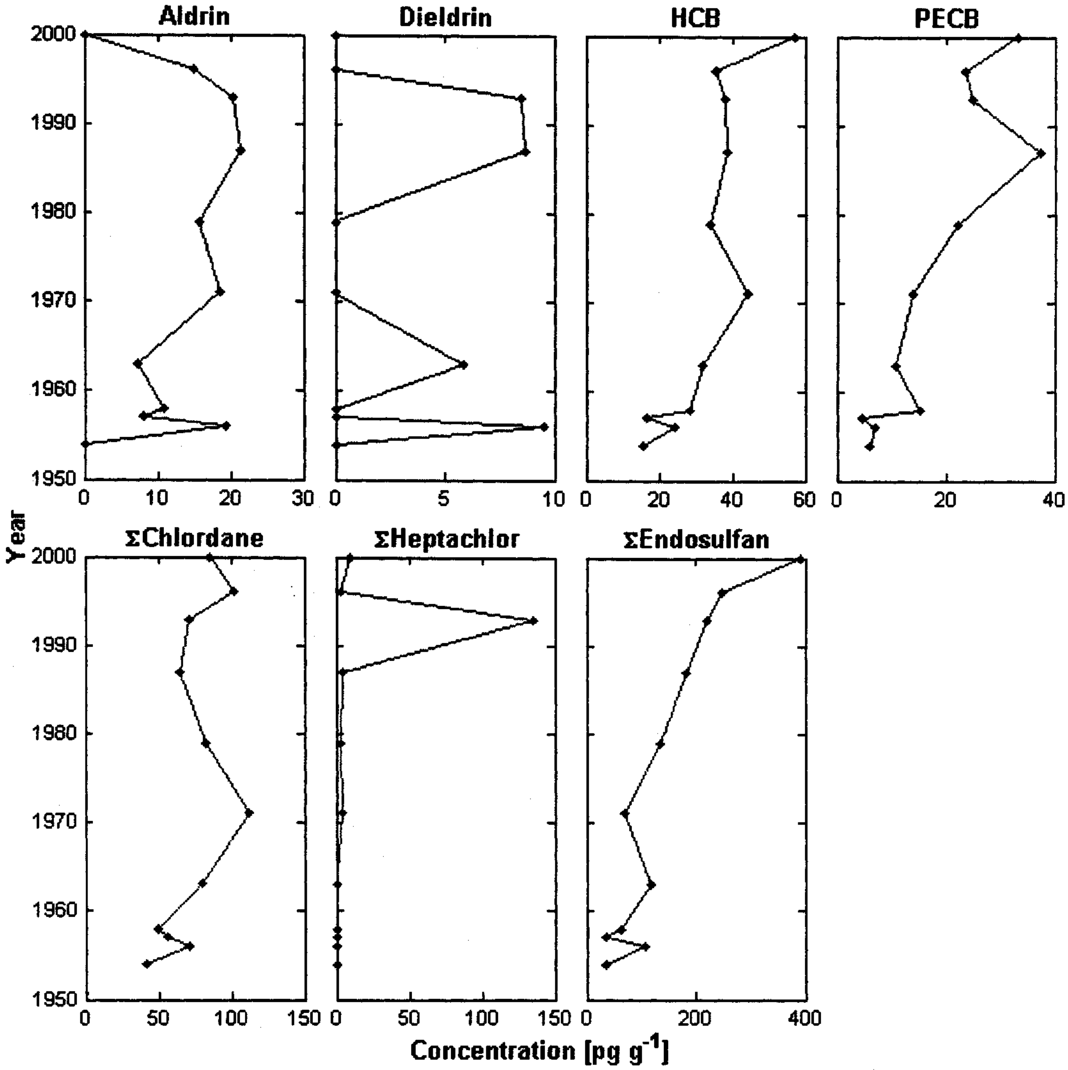


Figure D.5: Down-core profiles of concentrations of individual OC pestidices Aldrin, Dieldrin, HCB and PECB, and sums of chlordane, heptachlor, and endosulfan fluxes in Shuswap Lake.

D.3 Bowron Lake

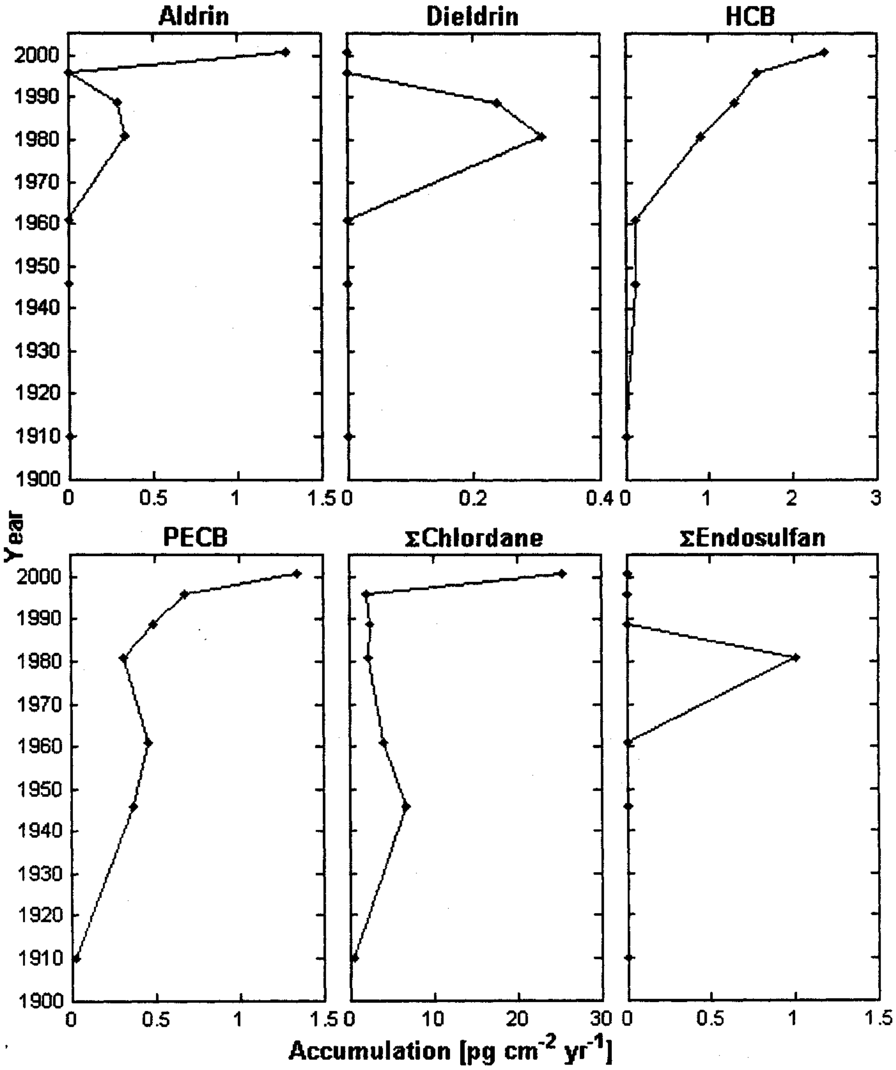


Figure D.6: Selected OC pesticide down-core fluxes in Bowron Lake sediments.

D.4 Quesnel Lake

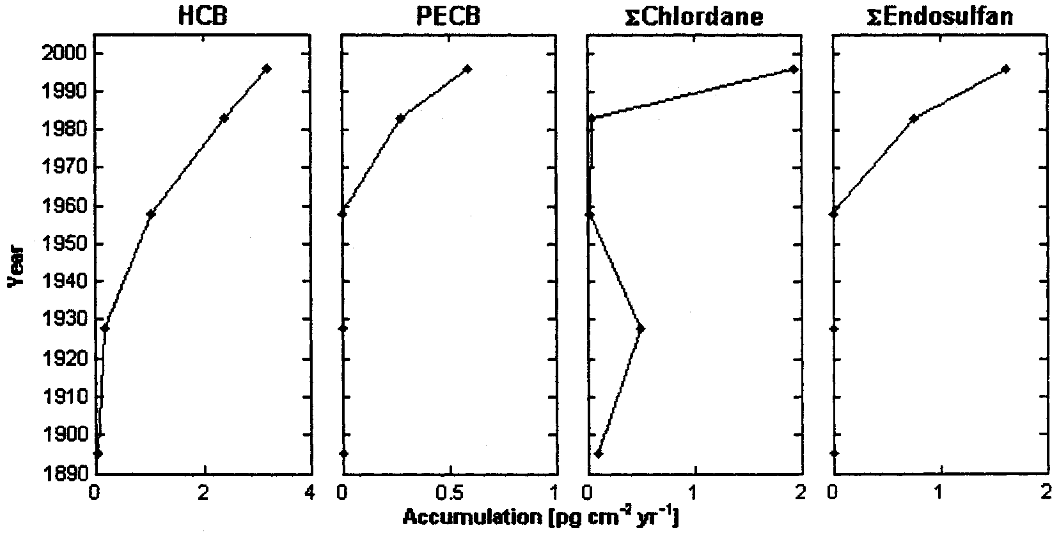


Figure D.7: Selected OC pesticide down-core fluxes in Quesnel Lake sediments.

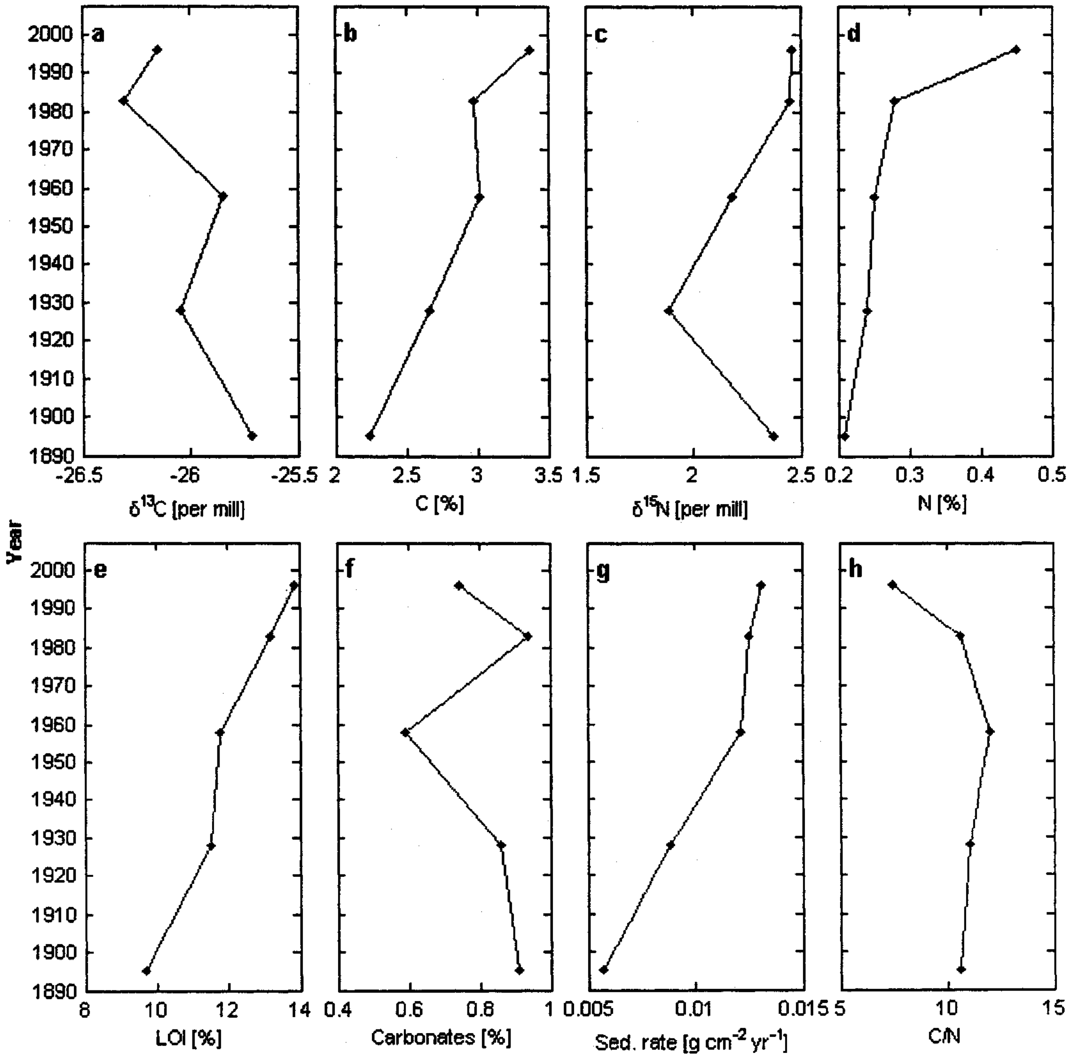


Figure D.8: Down-core profiles of a, δ^{13}C; b, percent carbon; c, δ^{15}N; d, percent nitrogen; e, percent organic matter (LOI); f, percent carbonates; g, sedimentation rate; h, C/N in Quesnel Lake.

D.5 Fraser Lake

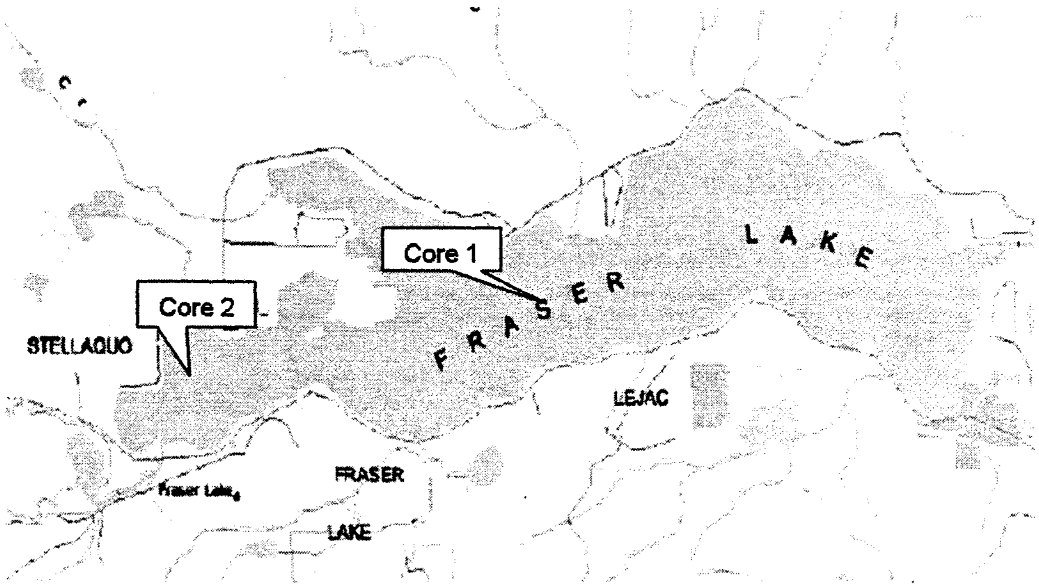


Figure D.9: A map of Fraser Lake in B.C., showing the approximate sampling locations of Core 1 and Core 2. The town of Fraser Lake is also indicated. The map was generated using the 'Fish Wizard' website provided by the Freshwater Fisheries Society of B.C. (http://www.fishwizard.com/).

D.6 Red Lake

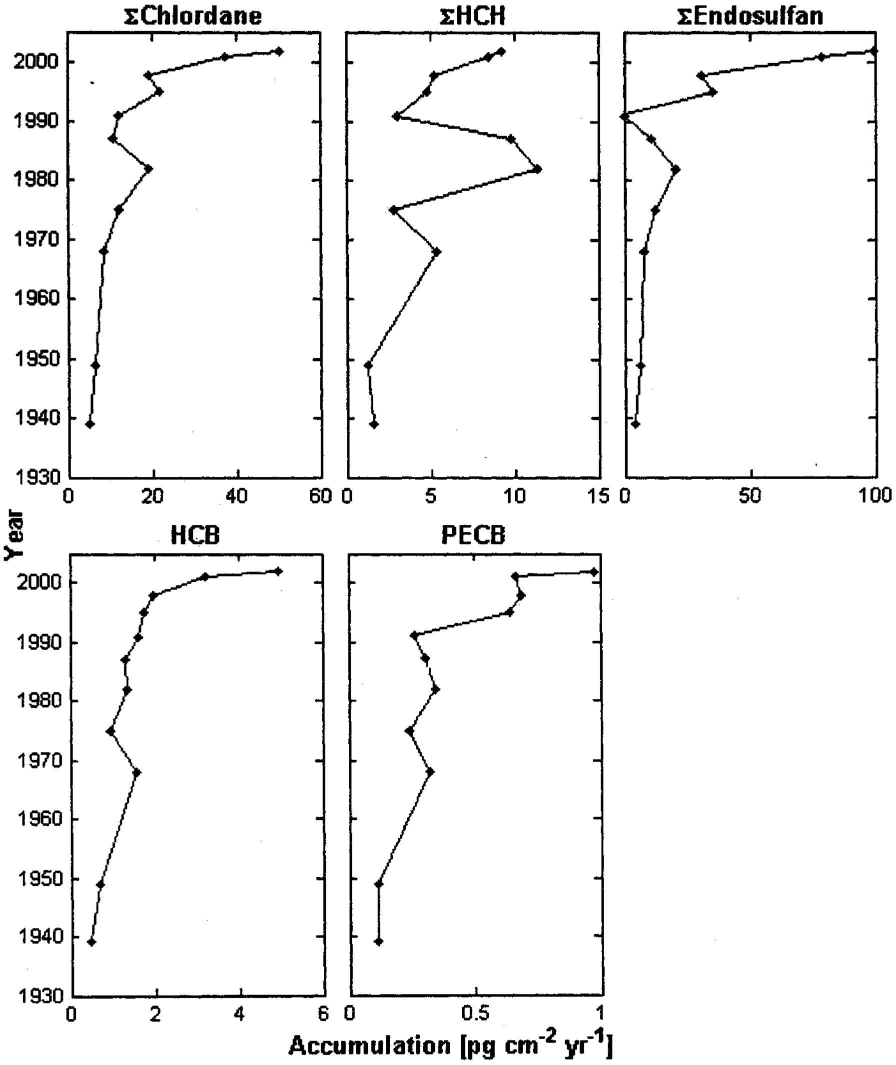


Figure D.10: Selected OC pesticide down-core fluxes in Red Lake sediments.

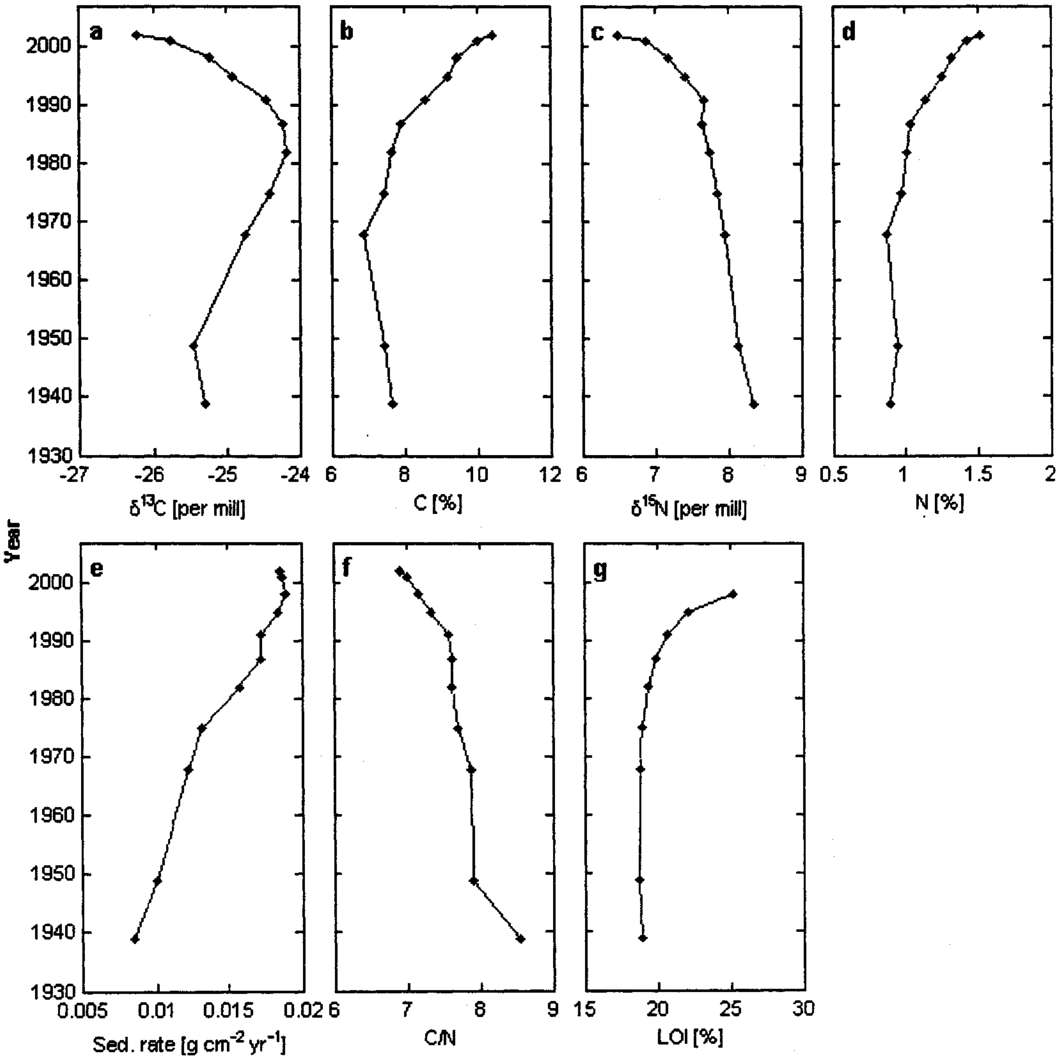


Figure D.11: Down-core profiles of a, δ^{13}C; b, percent carbon; c, δ^{15}N; d, percent nitrogen; e, sedimentation rate; f, C/N; g, percent organic matter (LOI) in Red Lake. Percent carbonates were not measured for this lake.

D.7 Upper Olga Lake

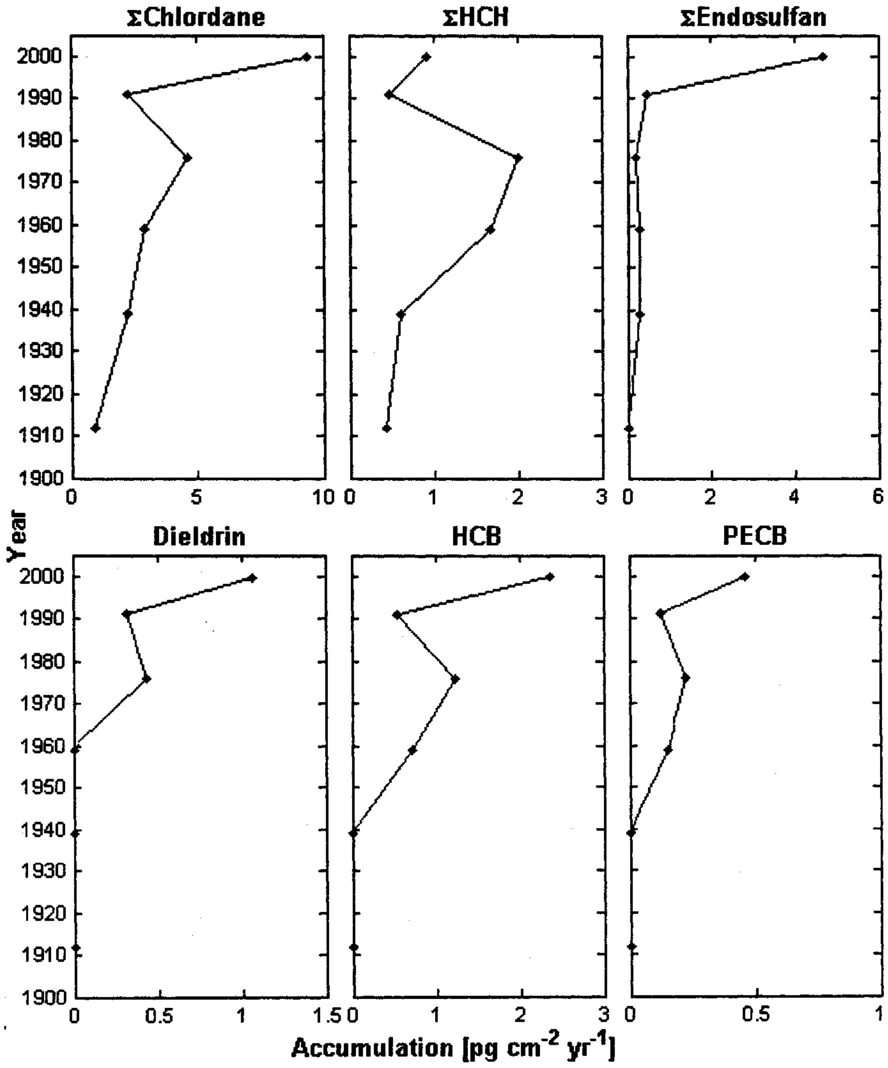


Figure D.12: Selected OC pesticide down-core fluxes in Upper Olga Lake sediments.

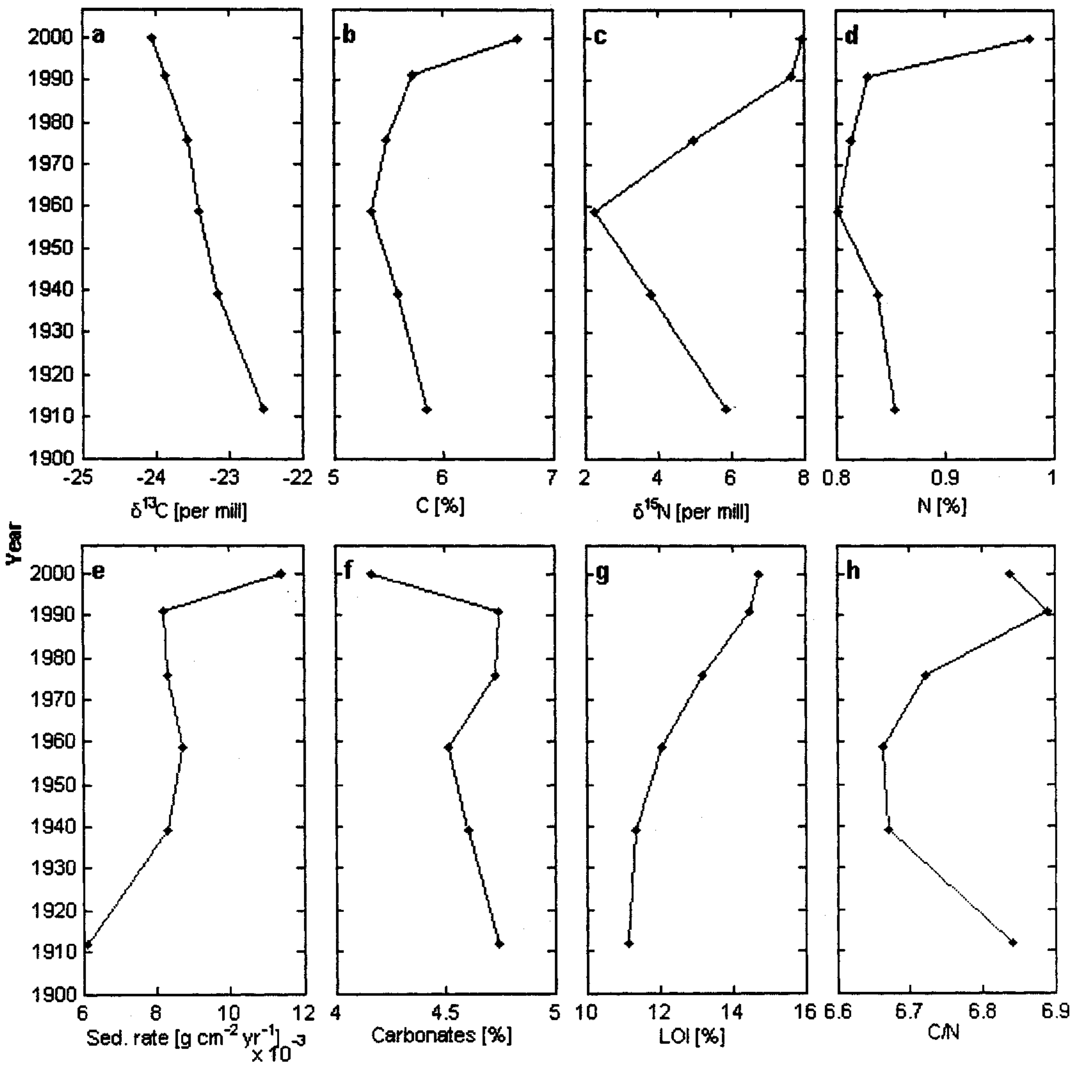


Figure D.13: Down-core profiles of a, δ^{13}C; b, percent carbon; c, δ^{15}N; d, percent nitrogen; e, sedimentation rate; f, percent carbonates; g, percent organic matter (LOI); h, C/N in Upper Olga Lake.

D.8 Frazer Lake

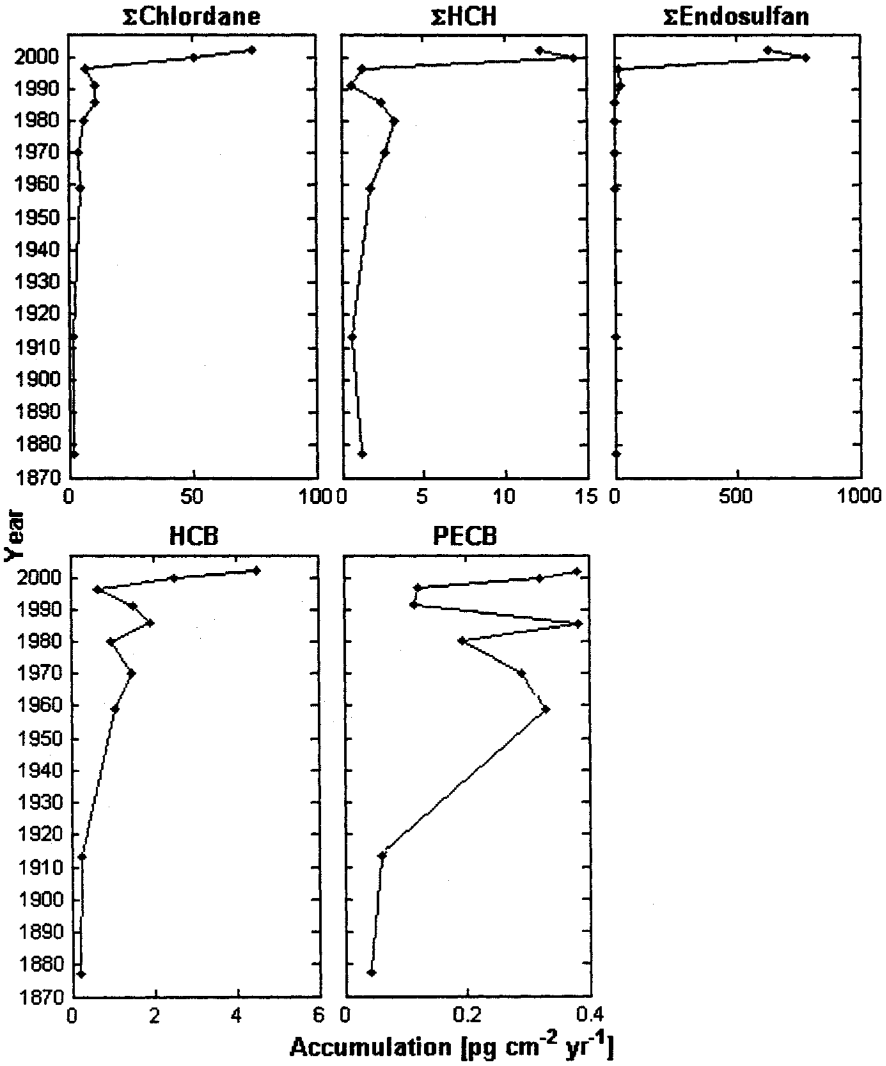


Figure D.14: Selected OC pesticide down-core fluxes in Frazer Lake sediments.

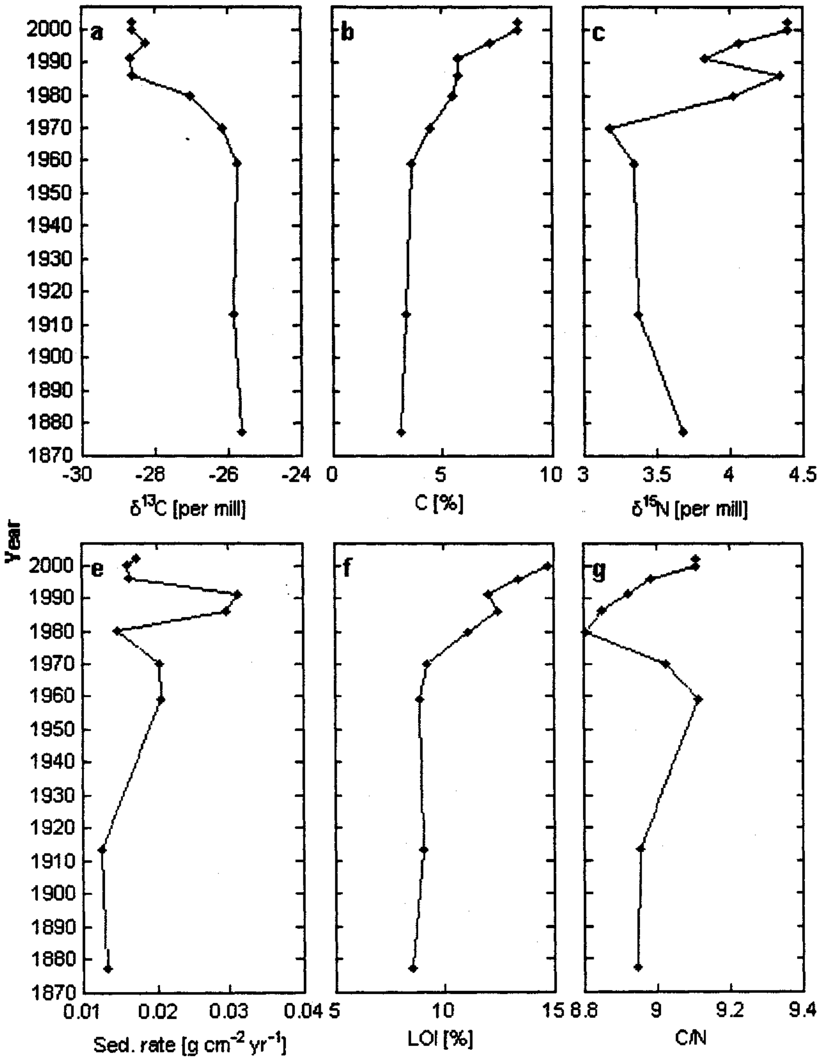


Figure D.15: Down-core profiles of a, δ^{13}C; b, percent carbon; c, δ^{15}N; d, percent nitrogen; e, sedimentation rate; f, percent organic matter (LOI); g, C/N in Frazer Lake. Percent carbonates were not measured for this lake.

D.9 Karluk Lake

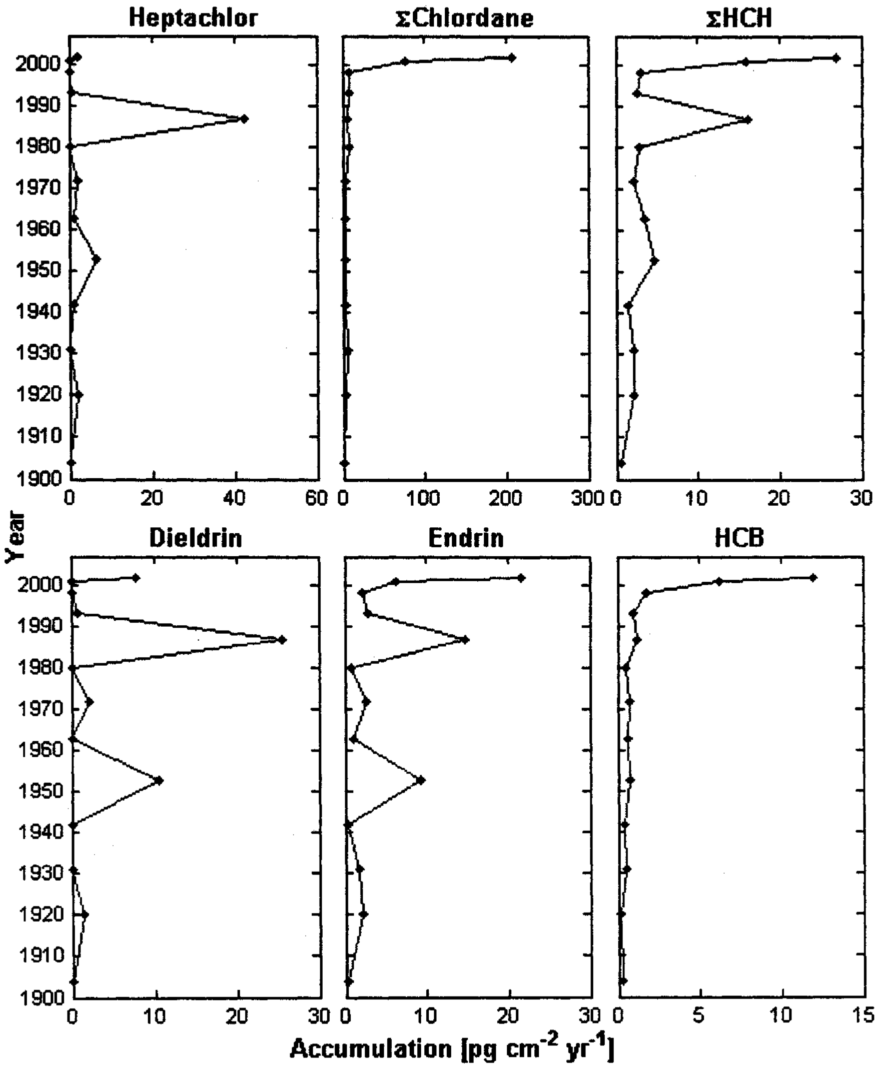


Figure D.16: Selected OC pesticide down-core fluxes in Karluk Lake sediments.

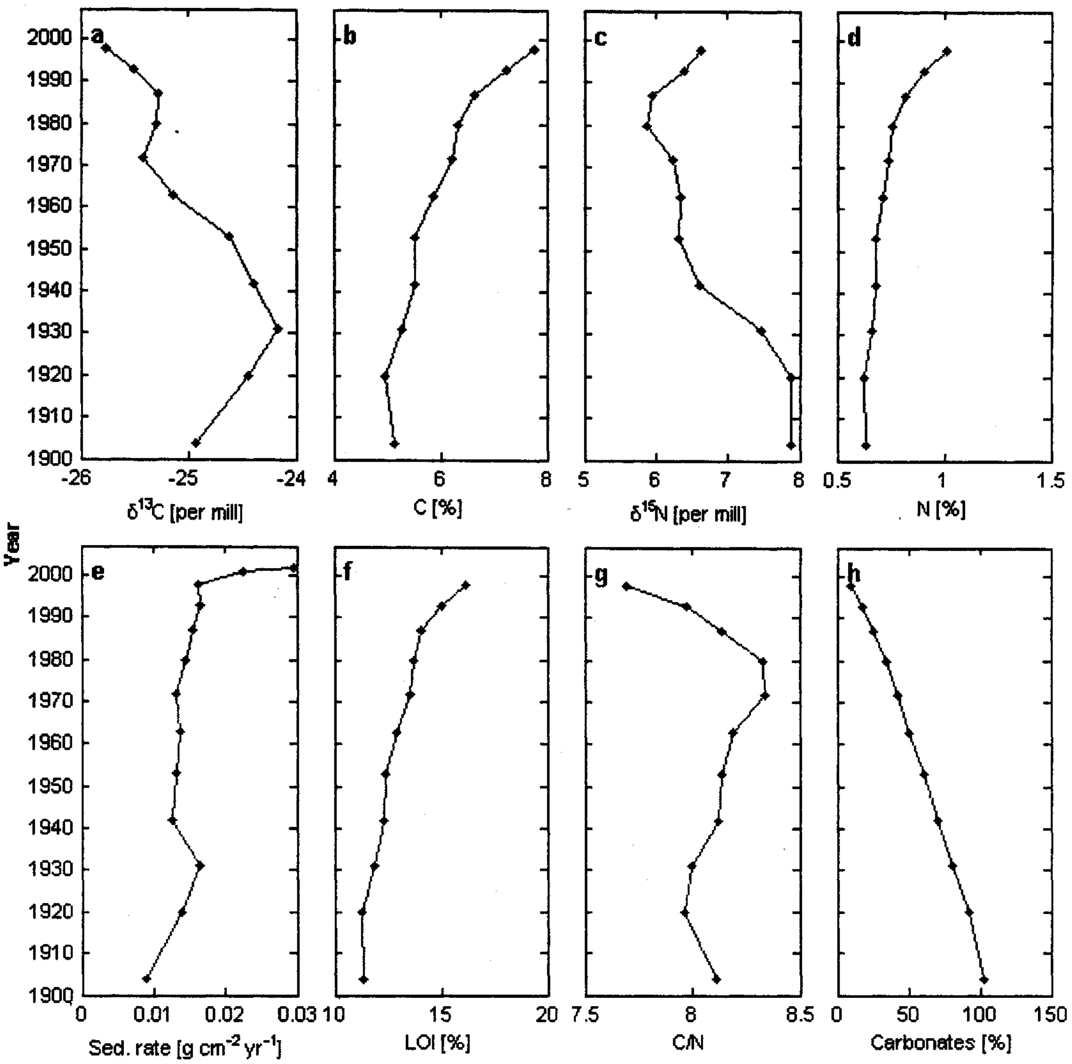


Figure D.17: Down-core profiles of a, δ^{13}C; b, percent carbon; c, δ^{15}N; d, percent nitrogen; e, sedimentation rate; f, percent organic matter (LOI); g, C/N; h, percent carbonates in Karluk Lake.

Appendix E

Discussion

Theoretical calculation of ΣPCB concentration input by sockeye salmon into Red Lake:
Average concentration of ΣPCB in whole sockeye salmon (measured in whole salmon, n=7): 4,500 ng/fish.
Yearly average of sockeye spawners to Red Lake (10-year average): 38,799 salmon km^{-2}.
ΣPCB load brought in by salmon:

$$\frac{4,500 * 38,799}{1,000,000} = 174.6 \text{ ng m}^{-2}\text{yr}^{-1}$$

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