

# **Late-run Sockeye at Risk: An Overview of Environmental Contaminants in Fraser River Salmon Habitat**

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V8L 4B2

2002

**Canadian Technical Report of  
Fisheries and Aquatic Sciences 2429**



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LATE-RUN SOCKEYE AT RISK:  
AN OVERVIEW OF ENVIRONMENTAL CONTAMINANTS IN FRASER RIVER  
SALMON HABITAT

by

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the Minister of Fisheries and Oceans.  
Cat. No. Fs 97-6/2429E ISSN 0706-6457

Correct citation for this publication:

Johannessen, D.I. and P.S. Ross. 2002. Late-run sockeye at risk: an overview of  
environmental contaminants in Fraser River salmon habitat. Can. Tech. Rep.  
Fish. Aquat. Sci. 2429: x + 108p.

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## ABSTRACT

Johannessen, D.I. and P.S. Ross. 2002. Late-run sockeye at risk: an overview of environmental contaminants in Fraser River salmon habitat. Can. Tech. Rep. Fish. Aquat. Sci. 2429: x + 108p.

Fraser River sockeye salmon (*Oncorhynchus nerka*) utilize some of the most populated and industrialized regions of British Columbia during sensitive life stages (e.g. spawning, egg hatching, larval development and migrations between fresh and salt water). During the period from 1994 to 2001, pre-spawning mortality of adults, associated with a change in migration timing, increased from 10% to over 90% among late-run stocks of Fraser River sockeye. It is estimated that this level of mortality could translate to lost production/harvest of approximately 5 million fish with an approximate value of \$50 million dollars in 2002 alone. A contaminant-associated impact represents one of several possible contributing factors touted in the sudden appearance of this mysterious phenomenon. Contaminants could be contributing to the disruption of migratory timing through a number of contaminant-related impacts, including a disruption of endocrine processes (e.g. permanent or transitory neurotoxicity or developmental toxicities) or interference with olfactory cues during migration. In this literature-based risk assessment, we review contaminant types, usage, and sources in late-run sockeye habitat, and prioritize contaminants of concern. Contaminants were prioritized based on whether there was evidence of increasing use, or sale, of the contaminant in sockeye habitat during the period in question. Where known, toxicity, sublethal effects, and other factors are also discussed. Based on this assessment, we conclude that there is a need for research into the exposure levels and effects of several key chemical classes of concern including: i) two classes of persistent organic pollutants (POPs): polybrominated diphenylethers (PBDEs) and phthalate esters; ii) the family of organic surfactants including alkylphenol ethoxylates (APEs) and their degradation products; iii) a number of agricultural and household pesticides which have seen increased use in B.C. during the 1990s, including metam sodium, formaldehyde, and chlorothalonil; and iv) the wood preservatives creosote, chromated copper arsenate, ammoniacal copper arsenate, and ammoniacal copper zinc arsenate. Also of concern are a number of contaminants for which almost no information exists, but are likely to be increasing in the environment, including pharmaceutical and personal care product chemicals, which enter waterways through sewage effluent. The lack of data on the concentrations of any of these contaminants in Fraser River late-run sockeye salmon stocks render it impossible to accurately assess the possible role of contaminants in the disruption of migratory timing in late-run sockeye stocks. However, our assessment does provide a listing of several contaminant classes of concern, and highlights the need for scientific research which i) characterizes contaminant types and concentrations in late-run sockeye, and ii) evaluates the toxicity of different priority chemicals to different stages of sockeye salmon.

## RÉSUMÉ

Johannessen, D.I. and P.S. Ross. 2002. Late-run sockeye at risk: an overview of environmental contaminants in Fraser River salmon habitat. Can. Tech. Rep. Fish. Aquat. Sci. 2429: x + 108p.

Le saumon sockeye du Fraser (*Oncorhynchus nerka*) est tributaire de plusieurs des régions les plus peuplées et industrialisées de la Colombie-Britannique pendant certains de ses stades de vie les plus sensibles (p. ex. le frai, l'éclosion des oeufs, le développement larvaire et les migrations entre l'eau douce et l'eau salée). Entre 1994 et 2001, la mortalité pré-frai, associée à un changement de l'époque de migration, est passée de 10 % à plus de 90 % parmi les stocks de remonte tardive du saumon sockeye du Fraser. On estime qu'un tel taux de mortalité pourrait se traduire par une perte de captures ou un manque à produire d'environ 5 millions de saumons dont la valeur se situe autour de 50 millions de dollars rien qu'en 2002. L'impact de contaminants représente un des facteurs contributifs possibles avancés pour expliquer l'apparence soudaine de ce phénomène mystérieux. Des contaminants pourraient contribuer à la perturbation de l'époque choisie pour la migration par le biais de divers impacts liés aux contaminants, en particulier des perturbateurs endocrines (p. ex. neurotoxicité permanente ou transitoire ou toxicités développementales) ou une interférence au niveau des signaux olfactifs durant la migration. Dans cette évaluation des risques fondée sur une analyse documentaire, nous effectuons un survol complet des types de contaminants, de leur emploi et de leurs sources relativement à l'habitat du saumon sockeye de remonte tardive et nous élaborons une liste prioritaire des contaminants d'intérêt spécial. Le principal critère d'inscription à la liste était la preuve d'une utilisation accrue dans l'habitat du saumon sockeye durant la période en question. On aborde également, lorsqu'on les connaît, la toxicité, les effets sublétaux ainsi que d'autres facteurs. Cette évaluation conclut qu'il est nécessaire d'entreprendre des recherches sur les niveaux d'exposition et sur les effets de plusieurs produits chimiques d'intérêt spécial dont: i) deux classes de polluants organiques persistants (POP): les éthers diphenyliques polybromés et les esters de phthalate; ii) la famille des agents de surface organiques qui comprend les alkylphénols éthoxylés et leurs produits de dégradation; iii) divers pesticides agricoles et ménagers dont l'utilisation s'est accrue en C.-B. tout au long des années 1990, notamment le métam-sodium, le formaldéhyde et le chlorothalonil; iv) les produits de préservation du bois suivants: créosote, arséniate de cuivre chromaté, arséniate de cuivre ammoniacal et arséniate de cuivre et de zinc ammoniacal. On s'intéresse aussi à plusieurs contaminants à propos desquels il n'existe pour ainsi dire aucune information, mais dont la concentration dans l'environnement est susceptible d'augmenter, notamment les produits chimiques pharmaceutiques et d'hygiène et de beauté qui pénètrent dans les cours d'eau sous forme d'effluents d'eaux usées. L'absence de données sur les concentrations de ces divers contaminants dans les stocks de saumon sockeye du Fraser de remonte tardive nous met dans l'impossibilité d'évaluer le rôle possible des contaminants dans la perturbation de l'époque migratoire des stocks de saumon sockeye de remonte tardive. Cependant, notre évaluation dresse la liste de plusieurs classes de contaminants d'intérêt spécial et souligne la nécessité d'entreprendre des recherches scientifiques i) caractérisant les types et les concentrations de contaminants dans le saumon de remonte tardive et ii) évaluant la toxicité de différents produits chimiques prioritaires à différents stades du cycle biologique du saumon sockeye.

## ACKNOWLEDGEMENTS

This project was funded through a grant from the Pacific Salmon Commission (PSC). The advice and support of Mike Lapointe, Jim Woodey and Don Kowal at various points during this project are gratefully acknowledged.

Sue Grant provided helpful advice and the resources that had been gathered for her report entitled "Southern resident killer whales at risk: toxic chemicals in the British Columbia and Washington environment" (Grant and Ross 2002).

The advice of numerous scientists and staff within Fisheries and Oceans Canada, Environment Canada, B.C. Ministry of Forests, and Washington Department of Fish and Wildlife are greatly appreciated.

The thoughtful reviews of earlier versions of this report by Sandra O'Neill, Steve Samis, Wayne Fairchild, Taina Tuominen, Stephanie Sylvestre, Doug Wilson, Robie Macdonald, and Reet Dhillon greatly facilitated the production of the final draft.

Many thanks also to Patricia Kimber for her graphical work on a number of figures.

# 1 INTRODUCTION

## 1.1 THE PROBLEM

Until recently, Fraser River late-run sockeye salmon (*Oncorhynchus nerka*) arrived in the Strait of Georgia on their spawning migration in mid-August. The sockeye then milled back and forth in the Strait and the Fraser River estuary for roughly six weeks before moving up the Fraser River towards their spawning grounds. This milling period began to decrease significantly in 1995, and, concurrent with the early entry, the sockeye exhibited unusually high pre-spawning mortality (Figure 1). This trend increased to the point where the milling period in 2000 and 2001 had decreased to a few days and the pre-spawning mortality had increased to more than 90%. If this trend continues unchecked, the late-run sockeye will experience a catastrophic population decline. The Pacific Salmon Commission (2001a) estimates suggest that the cost of this in fish harvest/production would be roughly 5 million fish or approximately \$50 million dollars in lost revenues in 2002 alone.

There is evidence that the actual mortality is caused by an infection of the myxosporean parasite, *Parvicapsula minibicornis*, in kidneys of affected sockeye individuals (Pacific Salmon Commission 2001a; Pacific Salmon Commission 2001c). However, it is believed that the infection would not progress to a lethal level prior to spawning, if the sockeye were not heading upstream earlier in the season (Pacific Salmon Commission 2001a). Thus, the key to the sockeye mortality is to find the cause of their early entry into the Fraser River.

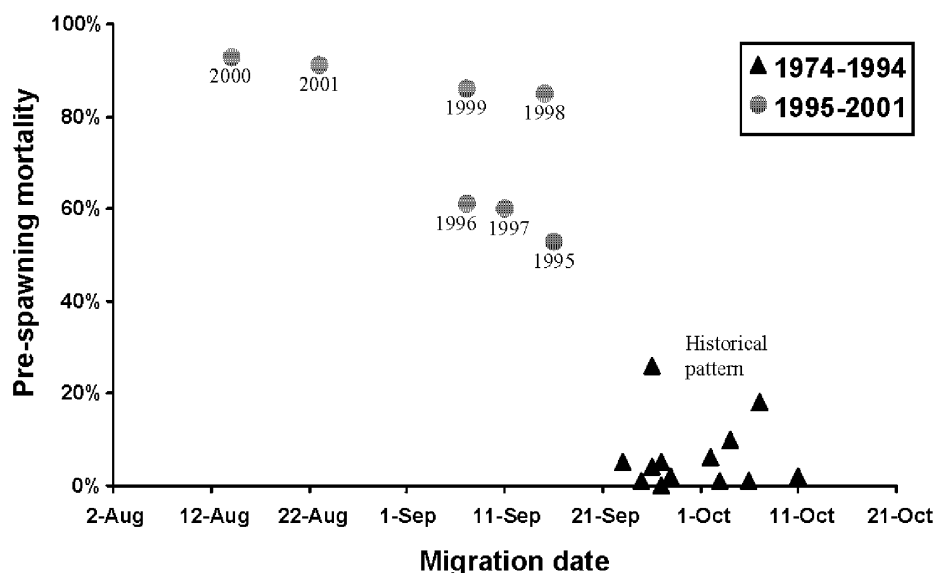


Figure 1. Relationship between peak migration date past Mission, B.C. and the mortality between Mission and the spawning grounds. Figure from: (Lapointe 2002).

## 1.2 FOCUS OF THIS REPORT

We hypothesize that if a contaminant is to have caused this change in behaviour, it must have increased in use sometime in the last 10 years. A survey of current literature has been carried out in order to assess and prioritize a variety of contaminants which might be the cause of this behaviour change. Prioritization is based first on the evidence of an increase in the contaminant's use within sockeye habitat, followed by information on lethal and sub-lethal toxicity and known effects of the contaminant on fish.

## 1.3 KNOWN CONTAMINANT EFFECTS ON FISH

The object of this study is not to identify contaminants that might be killing sockeye salmon. The goal is to identify contaminants that could alter the normal return migration timing pattern through sublethal effects. The following are recognised sublethal effects of some contaminants which could result in the observed behaviour change.

### 1.3.1 Neurotoxicity

Neurotoxicity can involve temporary alteration of nerve or brain function such as the acetylcholinesterase inhibition discussed below. These temporary effects can last months and affect behaviour in a variety of ways. Some contaminants such as polychlorinated biphenyls (PCBs) are more destructive and can cause permanent damage to the brain or nervous system. This damage can result from a low level, chronic exposure or a brief, acute exposure at any point in the life cycle. Genetically programmed behaviour, such as migration timing, is triggered by external stimuli which involves the brain and nervous system. For this reason, a neurotoxic effect is perhaps the most likely scenario for a possible contaminant-related basis for the observed change in sockeye behaviour.

#### 1.3.1.1 Acetylcholinesterase Inhibition

Many contaminants, notably the majority of organophosphate and carbamate pesticides, work through the inhibition of acetylcholinesterase (AChE). In the nervous system of vertebrates, as well as insects, acetylcholine is the chemical transmitter involved in the transmission of impulses across synapses. To stop the nerve continuing to transmit the signal, AChE breaks down acetylcholine immediately after it has had its effect. AChE inhibition causes the neuron to continue to be stimulated (Zinkl et al. 1991; EXTOWNET 2001; Murty 1986b). The effects of AChE inhibition in fish vary widely. Studies have shown that AChE inhibition as low as 8% can be lethal in some species while some fish are able to survive inhibition of 70-90%. Sublethal effects of AChE inhibition in fish can include: reproduction problems, reduced stamina, altered swimming and social interaction, flared opercula, hyperexcitability, and other behaviour changes (various sources cited in Gruber and Munn 1998). Recent work focused on olfaction in salmon note that AChE inhibition may interfere with the normal integration of chemical cues within the olfactory forebrain (Jarrard et al. 2001; Scholz et al. 2002). The loss of olfactory capacity could interfere with many important behaviours in salmon, including feeding, defence, schooling, reproduction, and migration (Scholz et al. 2000; Little et al. 1990; Brewer et al. 2001; Moore and Waring 1996).

### ***1.3.2 Direct Olfactory Effects***

Chemical imprinting has been shown to attract fish towards a spawning stream, suggesting that olfaction is connected to migratory behavior (Cooper et al. 1976; Hasler et al. 1983). Related to the olfactory disruption mentioned above, some compounds, notably the metals copper and cobalt, are known to affect olfaction and result in behaviour change. Chinook salmon and rainbow trout have shown avoidance behaviour to low levels of these metals (Hansen et al. 1999a; Hansen 1998). The antisapstain chemical TCMTB was shown to cause saltwater aversion (Kruzynski and Birtwell 1994). DDT has been shown to cause a preference for warm water by fish (Ewing 1999). There is also evidence that some contaminants can either mimic or mask biologically important odorants (Stone and Schreck 1994). Since olfaction is so closely tied with behaviour, any of the effects described here could account for a behaviour change.

### ***1.3.3 Endocrine Disruption***

The endocrine system is involved in the coordination of a wide variety of physiological functions including development, growth, reproduction, chemical balance (osmoregulation), and chemical messaging. Disruption of this system can affect behaviour and the timing and extent of changes in the body such as smoltification (Madsen et al. 1997). The main focus on this emerging issue in humans and wildlife has been related to the disruption of sexual development. Effects such as feminization, masculinization, and the production of vitellogenin (a precursor of egg proteins) in males have been documented in fish (Janz et al. 2001; Lange et al. 2001; Knudsen et al. 1997; Jobling et al. 1998; Gimeno et al. 1996; Panter et al. 2000; Rogers-Gray et al. 2000). There are therefore a variety of ways in which disruption of the endocrine system could lead to the observed behaviour change in sockeye salmon.

### ***1.3.4 Osmoregulatory Disruption***

A number of contaminants have been shown to impair the osmoregulation and maintenance of ionic balance in fish (Staurnes et al. 1996; Johnston et al. 1998; Lehtinen et al. 1990; Pinkney et al. 1989). Osmoregulation is particularly complex for salmon because they are anadromous (life cycle involves both fresh and salt water), therefore their process of osmoregulation must change dramatically as smolts and again as returning adults. The observed behaviour change in the Fraser River late-run sockeye occurs just at the time when this process is switching from salt to fresh water operation. Furthermore, work by Tony Farrell and Ed Donaldson has found evidence of osmoregulatory stress in these salmon after entering the Fraser River (Pacific Salmon Commission 2001c; Pacific Salmon Commission 2001b). It is possible that a contaminant (or combination of contaminants) could disrupt the osmoregulatory changeover such that the salmon would need to get into freshwater as soon as possible rather than waiting for the usual migration trigger.

### ***1.3.5 Immunosuppression***

Recent work has shown that exposure to toxic contaminants can reduce the effectiveness of an organism's immune system thus making them more susceptible to disease and

parasitism. This has been shown to be true for Pacific salmonids (Arkoosh et al. 1998; Arkoosh et al. 1991). It is not clear how this sublethal effect might alter salmonid behaviour. However, since the ultimate mortality of these salmon is attributed to a parasite, the impairment of immunity may be a contributing factor in their death. It has also been postulated that the behaviour change may be a direct or indirect result of the parasitic infection (Pacific Salmon Commission 2001c; Pacific Salmon Commission 2001b).

#### ***1.3.6 Developmental Effects***

Early life stages of aquatic organisms can be more susceptible to some of the effects described above such as neurotoxicity and endocrine disruption. Persistent and bioaccumulative contaminants can be passed from the female to the eggs and therefore be present right from the beginnings of development. Behaviour of an organism is the result of a complex interaction between stimuli, communication systems, the brain, and the muscles that carry out the response. Problems in the development of any of these systems could result in immediate or future behavioural abnormalities.

### **1.4 EXPOSURE SCENARIOS**

Assuming that contaminant exposure represents a contributing factor to the observed behaviour change in late-run sockeye, a number of possible mechanisms may explain this. The exposure could take place at any stage in the life cycle prior to returning to the Fraser River. The exposure could be via food (lipophilic and bioaccumulative contaminants) or via the gills, skin absorption, or sensory exposure (hydrophilic contaminants in the water column). The exposure could cause a permanent change which results in the behaviour observed later in life, or could cause a temporary effect at, or shortly before, the time of the observed behaviour. A toxic effect may also be caused by a combination of contaminants, some of which may be catalysts or have the necessary effect only in combination. The following are a few of the possible contaminant exposure scenarios that could lead to the early upstream migration of the Fraser River late-run sockeye:

1. Salmon eggs, alevins and/or fry are exposed to chemicals in their microenvironment or spawning habitat that affect their long term development;
2. Salmon smolts are exposed to chemicals in their food or environment in the freshwater, estuarine, and coastal habitats which lead to long term effects;
3. Salmon juveniles and adults are exposed to chemicals through the consumption of prey in coastal B.C. and the North Pacific Ocean which lead to long term effects;
4. Returning adults are exposed to chemicals as they enter the Strait of Georgia or Fraser River plume, causing an almost immediate behavioural response.

Some participants at the Pacific Salmon Commission Workshops convened on this issue (Pacific Salmon Commission 2001c; Pacific Salmon Commission 2001b) thought the fourth scenario was the most likely if contaminants were to blame. However,



toxicological literature suggests that all of these scenarios could explain the observed behaviour change.

Population level effects on salmon have been attributed to contaminants in Europe and Canada prior to this issue. Researchers on Canada's east coast (Fairchild et al. 1999) have proposed that the forestry applied pesticide additive nonylphenol is the cause of Atlantic salmon catch declines as a result of its endocrine disrupting capabilities. Extensive efforts have been made to clean up the Great Lakes because of concerns about contaminant effects on a wide range of organisms including salmon (Norstrom et al. 1978). Reproductive impairment in European salmon, known as M-74 syndrome, is believed to be the result of exposure to contaminants such as dioxins and dioxin like pollutants (Norrgrén 1993).



## 2 FRASER RIVER SOCKEYE LIFE HISTORY

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The following is a general summary of Fraser River sockeye life history with some note of differences for the late-run stocks where necessary. There is a focus on migration behaviours and proposed migration mechanisms during various life stages in order to underline the complexities and uncertainties of the late-run return migration issue. Most of the information is summarized from three detailed life history documents (Gustafson et al. 1997; Pearcy 1992; Burgner 1991).

### 2.1 INCUBATION AND EMERGENCE

The spawning grounds of the late-run stocks are shown in Figure 2. Most sockeye in the Fraser River system deposit their eggs in tributary streams, trunk streams between lakes, and at lake outlets. One notable exception is in the case of Cultus Lake stocks, which also exhibit lake-beach spawning behaviour. The eggs are deposited in redds, or nests, which are shallow depressions in the gravel substrate that are covered over after egg deposition and fertilisation. Of the five Pacific salmon species, sockeye eggs exhibit the longest incubation period (up to 65 days to reach 50% hatch at a constant temperature of 10°C). Actual water temperatures in the wild vary with time and location but according to Burgner (1991): "...in general, spawning occurs during periods of declining temperatures in late summer or autumn, development occurs during winter at lowered temperature, and emergence ensues during rising water temperatures.". Sockeye that emerge with some yolk still attached tend to be those who must spend more time and energy to reach nursery areas (Burgner 1991 after Brannon 1972), which illustrates the evolution of genetic traits specific to a given stock. These fish with yolk attached are referred to as alevin and are called fry when the yolk is used up. The majority of the Fraser River sockeye migrate to lakes for one to two years of freshwater rearing. A few stocks, such as the Harrison River rapids, migrate to the ocean in the same year as emergence, usually after spending some rearing time in the Fraser River estuary. Sockeye exhibit a wide range of fry migration patterns due to the variety of situations encountered by the various stocks. Fry emerging from lakeshore redds at Cultus Lake simply move offshore into deeper water. Fry emerging from terminal or lateral tributary streams move downstream with the current into the nursery lake. Fry emerging from lake outlet streams usually swim upstream right away to reach the nursery lake. There are a few even more complex variations. Each of these different patterns of migration seem to be related to genetic differentiation between stocks. Observations of six Fraser River tributary fry populations led to the conclusion: "that mechanisms controlling sockeye fry migration are genetically based, and involve racially specific velocity response patterns, with olfactory stimulation having a directing influence on rheotactic behaviour. In the presence of current, light and temperature [seem to] influence only [the] timing and intensity of responsiveness. Once sockeye fry enter the lake environment, in the absence of current, light appears to become the major phenomenon directing orientation." (Burgner 1991 after Brannon 1972).

In the lake environment it is thought that orientation is done by the sun (celestial) when possible, and by the earth's magnetic field during times of darkness and heavy overcast (Burgner 1991 after Quinn 1982). Once again in the freshwater rearing habits, the Fraser

River salmon exhibit a wide variety of behaviours. Many other stocks feed for a month or so in the littoral areas of lakes before moving to deeper water. Some Fraser River stocks do this (Chilko and Shuswap lakes) while others skip the littoral residence (Cultus Lake) and some combine the two (Fraser Lake) (Burgner 1991 after Goodlad et al. 1974). What is nearly universal for the Fraser River stocks is smoltification after one year of lake residence with a few carry-overs for another year (Burgner 1991 after Killick and Clemens 1963). The migration from emergence to the rearing area is essentially an individual effort by each salmon fry. The fry begin showing schooling behaviour once in the rearing area and this continues through the remainder of the salmon's life cycle.

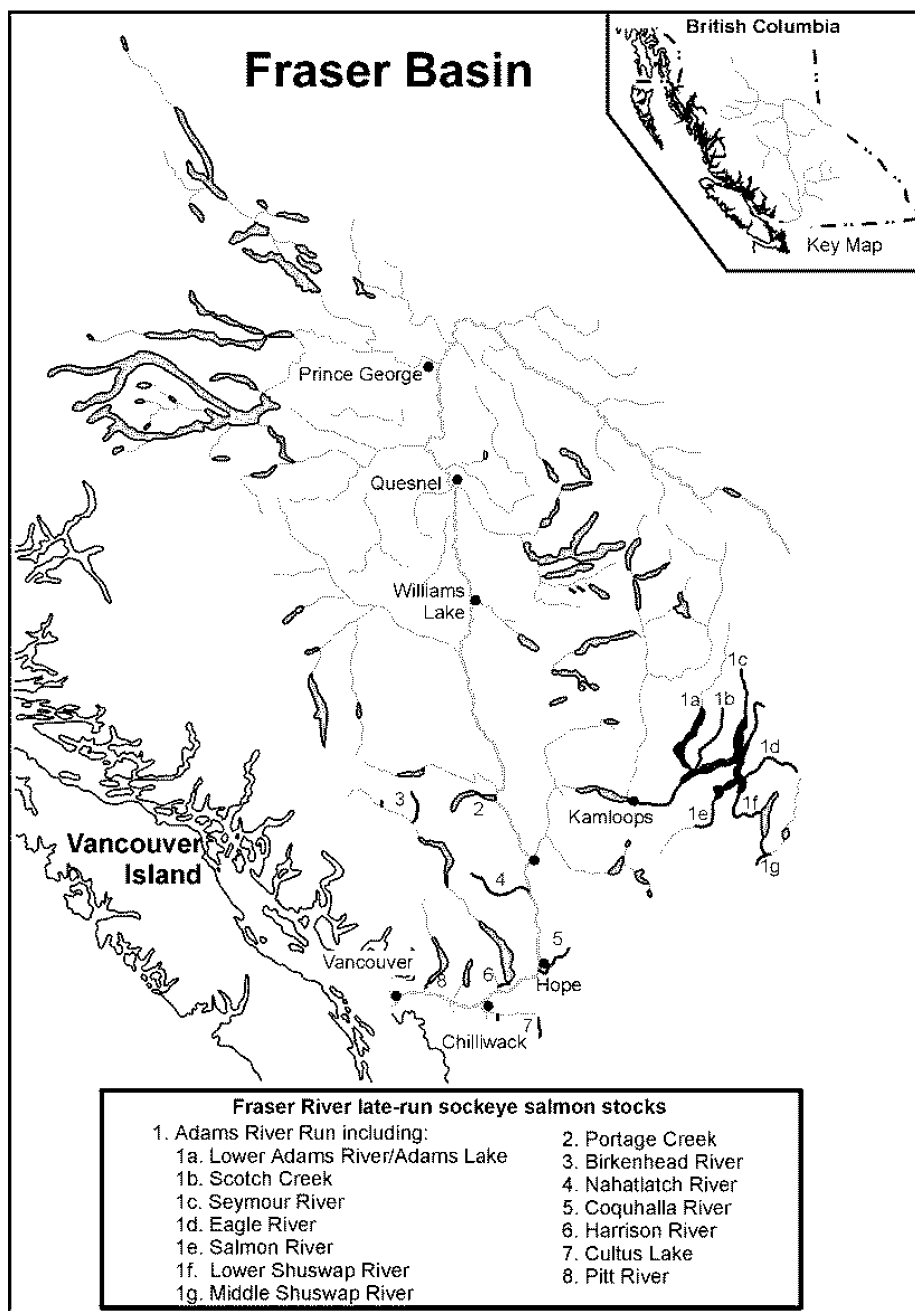
## 2.2 SMOLTIFICATION

Smoltification is the term applied to the preparation of the salmon for its migration from fresh to salt water. Burgner (1991) modifies Groot's (1982) summary of the major points as follows:

1. There is a strong endogenous component involved in triggering the diel and seasonal morphological, physiological, and behavioural changes during transformation from parr [fry] to smolt.
2. This endogenous rhythm only results in transformation when the juvenile sockeye reach a certain size (physiological age).
3. Daily photoperiod increase entrains the endogenous rhythm and thus controls the onset of smolting.
4. Temperature influences the onset of smolting through growth and regulates the magnitude and duration of the smolting process.
5. Hormones act as chemical links between the organism and the environment.
6. Hormone activities are rhythmic (circadian) and their effect on the fish depends on the phase relationship of their peaks of activity.
7. Entrainment of the hormonal rhythms to the diel cycle is through photoperiod, whereas the temporal relationship of the different rhythms is set by temperature.
8. The co-ordination of smolting processes leading towards migration readiness is attained in different ways for separate stocks as a result of adaptations to environmental factors operating in the habitat.

The timing of smolt migration is strongly linked to temperature such that in most lakes it begins shortly after ice breakup. This means that migration timing begins earliest at lakes that are in a warmer southern climate and progresses later as you move to colder and more northerly lakes. The migration itself varies in complexity between stocks and again the sockeye demonstrate unusually well developed navigational capability (Burgner 1991 after Hoar 1976).

Yearling Fraser River smolts enter the Strait of Georgia in April and May. The smolts first concentrate around the Fraser River mouth and by late May they have dispersed north along the mainland coast and west towards the Gulf Islands. Most leave the Strait of Georgia in late June and July via the northern passages. Their migration rate through



**Figure 2. Spawning areas of the Fraser River late-run sockeye stocks. Spawning areas modified from: (Fraser River Aboriginal Fisheries Secretariat 1999).**



the Strait of Georgia is estimated at 6-7 km/day (Burgner 1991 after Groot and Cooke 1987). They then migrate north-westward along the coast of British Columbia and Alaska.

Areas such as the Harrison River (below the rapids) produce salmon fry which do not spend a year in fresh water. These sockeye fry are called underyearling in comparison to the year old (yearling) smolts. These fry follow the smolts into the Strait of Georgia in late July having spent as much as five months in the marshes and sloughs of the Fraser River Delta. They remain spread throughout the Strait of Georgia through August and September by the end of which they have reached a size comparable to the yearling smolts. It is not known exactly when these underyearling sockeye leave the Strait of Georgia.

### **2.3 OCEAN MIGRATION**

After entering the open ocean during their first summer, the juvenile smolts remain in a band relatively close to shore. By July this band stretches roughly 1,800 km from Cape Flattery on the Olympic Peninsula to Yakutat in the Gulf of Alaska (Figure 3) but is still no more than 40 km offshore. Offshore movement is conjectured to take place in late autumn or winter based on the location of fish caught in the spring of the following year. The sockeye then spend usually 2 years moving in a counterclockwise oval around the Pacific Ocean (Figure 3) such that they are further north in the summers and further south in the winters.

### **2.4 RETURN MIGRATION AND SPAWNING**

When the salmon are mature enough to begin the return migration, they break off from the oval and head towards the coast and south towards the Fraser River. The salmon enter the Strait of Georgia via both Johnstone Strait and Juan de Fuca Strait. The percentage of salmon using the northern route versus the southern (called the Johnstone Strait diversion) has varied from less than 10% to over 80% (Groot and Quinn 1987). The diversion is believed to be a result of a combination of ocean environment factors during the time just prior to the initiation of migration (Groot and Quinn 1987; Xie and Hsieh 1989).

It is at this point that the Fraser River late-run sockeye have developed an unusual behaviour trait. The late-run sockeye arrive in the Strait of Georgia around mid-August with a number of other salmon stocks. Most of the other salmon move into the Fraser estuary and begin moving up the Fraser River within days of this arrival. The late-run sockeye traditionally mill around the southern Strait of Georgia (Figure 4) for 4 to 6 weeks before initiating the fresh water stage of their migration. It has long been recognised that many salmonids, and sockeye in particular, exhibit highly complex migration routes and timing (Pearcy 1992; Burgner 1991 after Gilhousen 1960). It has been hypothesised "that salmon navigate using a map, based on the inclination and declination of the earth's magnetic field, a celestial compass with a backup magnetic compass, and an endogenous circannual rhythm adjusted by daylength." (Burgner 1991 after Quinn 1982). Photoperiod (daylength) has been shown to influence the onset of osmoregulatory ability during smoltification (Clarke et al. 1981). The existence of a biological chronometer was also postulated as necessary if salmon are to use the sun's

position as a navigational reference (Hasler et al. 1958). The significance of this is that in order for the late-run sockeye to perform a temporally small variation in migration with such consistency, there must be a fairly accurate time awareness. Alteration or impairment of this timing ability would be a plausible explanation for the observed sockeye behaviour change.

Finally, in late September and early October, the late-run sockeye migrate up the Fraser River to their respective spawning grounds (Figure 2), spawn and die.



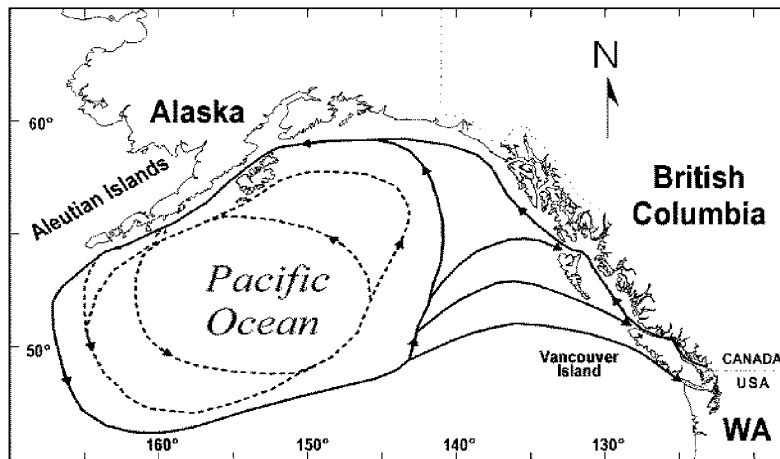


Figure 3. The open ocean migration pattern of Fraser River sockeye salmon. Grey area is overall distribution, black lines are main routes and dashed lines indicate other area covered (Migration patterns modified from French et al. 1976 and Healy 2002).

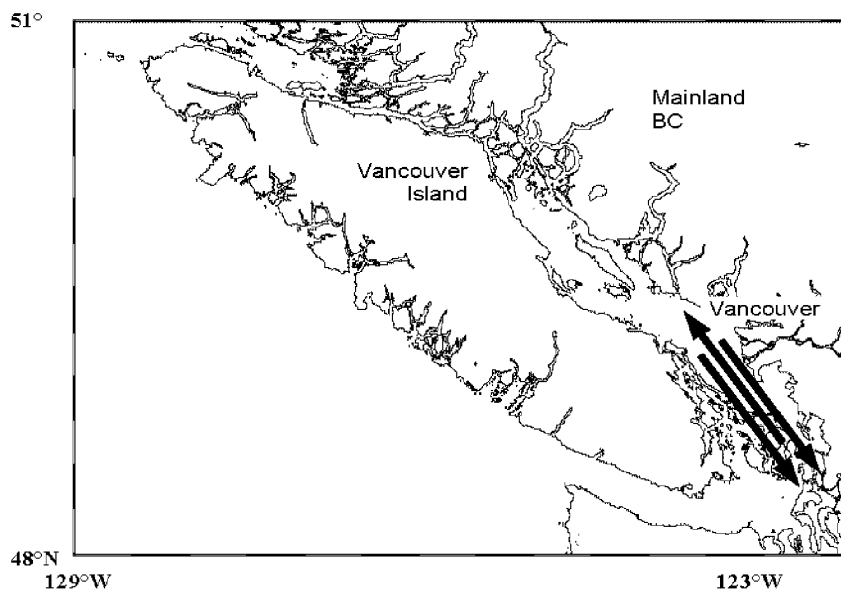


Figure 4. Black arrows indicate approximate milling pattern (Fraser River Sockeye Public Review Board 1995) of Fraser River late-run sockeye (Map modified from Schlitzer 2001).



### 3 POINT SOURCE POLLUTION

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#### 3.1 LAND USE

Approximately 83% of the people living within the Fraser Basin are concentrated near the mouth of the Fraser River (Lower Mainland) (Schreier et al. 1991). The 1994 population estimate for the Fraser Basin was 2.4 million of which 2 million lived in the Lower Fraser Valley (Nener and Wernick 1997). In 1996, the Fraser Basin contained 5,100 km<sup>2</sup> of urban area, 1,510 km<sup>2</sup> of agricultural area, 60% of B.C.'s metal mines and eight pulp and paper mills (Gray and Tuominen 1999). Figure 5 shows the layout of urban vs. agricultural land use for the Fraser Valley, Georgia Basin and Puget Sound.

Pulp mills have been estimated to discharge 38% of all the effluents going into the Fraser River Basin during the late 1980s and 90s. The majority of this effluent is from the six pulp mills located upriver of Hope at Prince George, Quesnel, and Kamloops (Figure 6). The two mills in the lower Fraser are small volume mills. Another 26% of discharge comes from industries other than pulp mills. Annacis and Lulu Island municipal waste water treatment plants (WWTPs) account for 27% themselves (Figure 7) with other municipal WWTPs contributing 9%. Note that Iona Island WWTP is not included in the assessment by McGreer and Belzer (1999) since it discharges into the Strait of Georgia. It is clear from this that, by volume, pulp mills and WWTPs are the major contributors to point source effluent in the Fraser Basin and projected population increase in the Greater Vancouver area will make the WWTP contribution more significant.

#### 3.2 MUNICIPAL WASTEWATER

Municipal wastewater can include domestic, industrial and commercial wastes as well as surface runoff from storm drains. Older systems combine all these wastes into one stream sent to the WWTP. In these systems, storm events can overload the system causing effluent to be directed to combined sewer overflows (CSOs) which discharge untreated wastes directly to the aquatic environment. Newer systems separate the waste waters from stormwater runoff which improves the treatment of the waste waters. However, this means that stormwater is discharged directly to the aquatic environment with no treatment. Stormwater contains a wide variety of pollutants washed from urban surfaces such as pesticides, heavy metals, polycyclic aromatic hydrocarbons (PAHs) and a variety of atmospherically deposited pollutants. Depending on the plant, WWTPs can provide pre-treatment, primary, secondary and/or tertiary treatment to the effluent. Each of these treatment levels provides progressively greater removal of solids, metals and certain contaminants. Pre-treatment is simply a screening out of solid material. Primary treatment mostly involves removal of solids that can be settled out or floated and skimmed off. Secondary treatment involves assisting in biological breakdown of organic matter. Tertiary treatment can involve chemical treatment and a variety of filtration techniques to remove even more contaminants. While there is no doubt that waste water treatment is an important step in the reduction of human pollution of the environment, there are three caveats that come with increasing treatment levels. First, the greater the treatment, the greater the quantity of sludge produced that must then be treated before it can be disposed of. This sludge is known to contain a variety of contaminants including

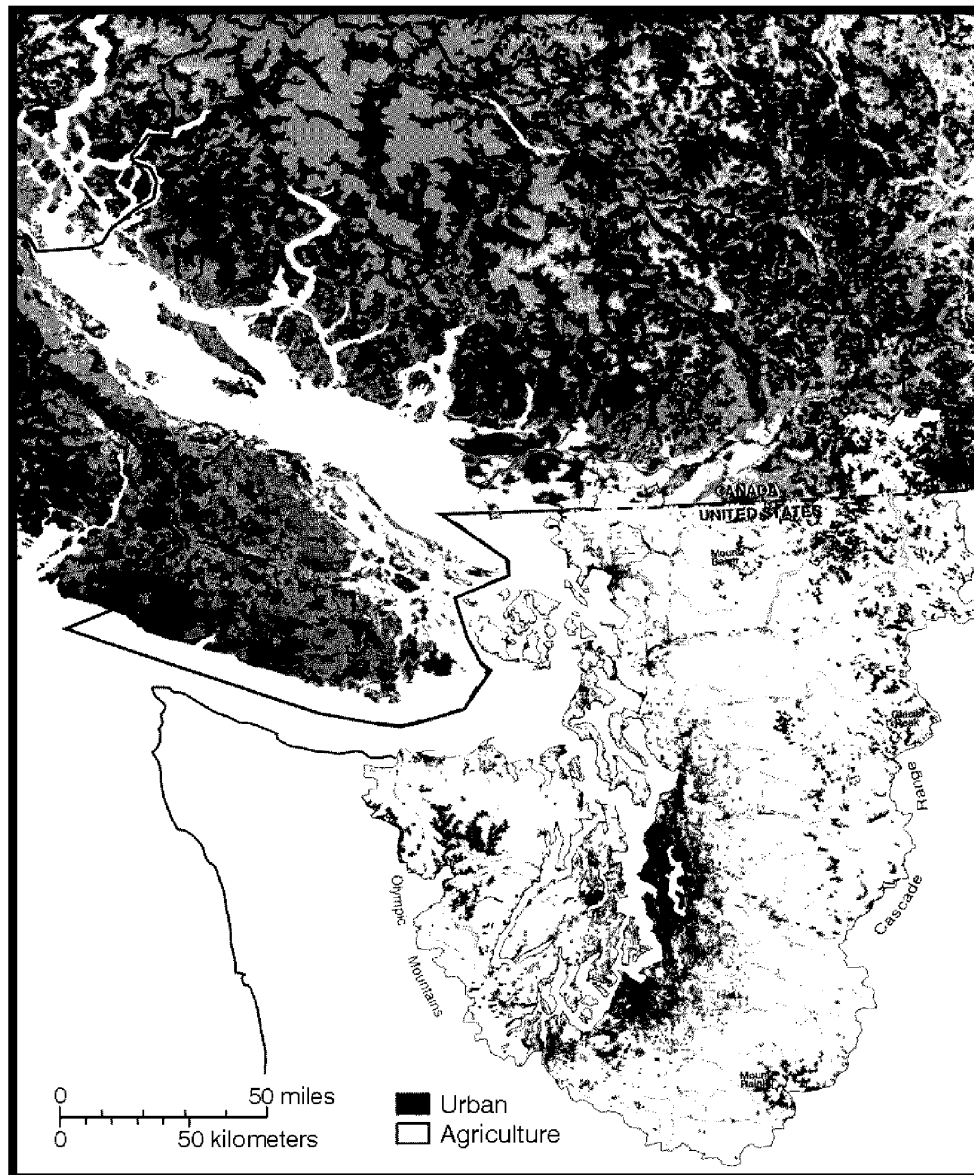
PCBs and other toxic and persistent compounds. Many of the more recent contaminants of concern are not yet tested for in sewage sludge and yet the sludge is often used as soil treatments (e.g. fertilizer) in forestry and agriculture where these contaminants can later migrate into local surface waters. Vancouver WWTPs produce 70,000 tonnes of sludge per year that is recycled and marketed as Nutrifor™ (Bertold and Stock 1999). The second caveat is that the breakdown of some contaminants leads to chemicals that are more toxic and more persistent. For example a number of pesticides, and the commonly detected surfactants alkylphenol ethoxylates, break down to products that have more of a negative impact than the parent compound (discussed in detail in sections 6.5, 6.6 and 12.2.2). The third caveat is that highly water soluble contaminants may not be affected by anything less than tertiary treatment.

### ***3.2.1 Fraser Basin Upstream of the Pitt River***

According to Environment Canada (Environment Canada 1997a), 150,000 m<sup>3</sup>/day of sewage effluent is discharged to the Fraser River Basin from 87 treatment plants upstream of Langley. Environment Canada monitored 15 of these WWTPs throughout the sub-basins of the upper Fraser. All but three of these facilities used secondary treatment. Tests made during the study showed that acute toxicity increased between 1992 and 1996 from 49% to 55% of the effluents registering as toxic. The conclusion was that secondary treatment reduces conventional parameters such as biological oxygen demand (BOD) and total suspended solids (TSS) but that these may not be the primary source of toxicity. The increase in effluent toxicity with time is thought to be a result of increasing population pressure on the facilities (McGreer and Belzer 1999).

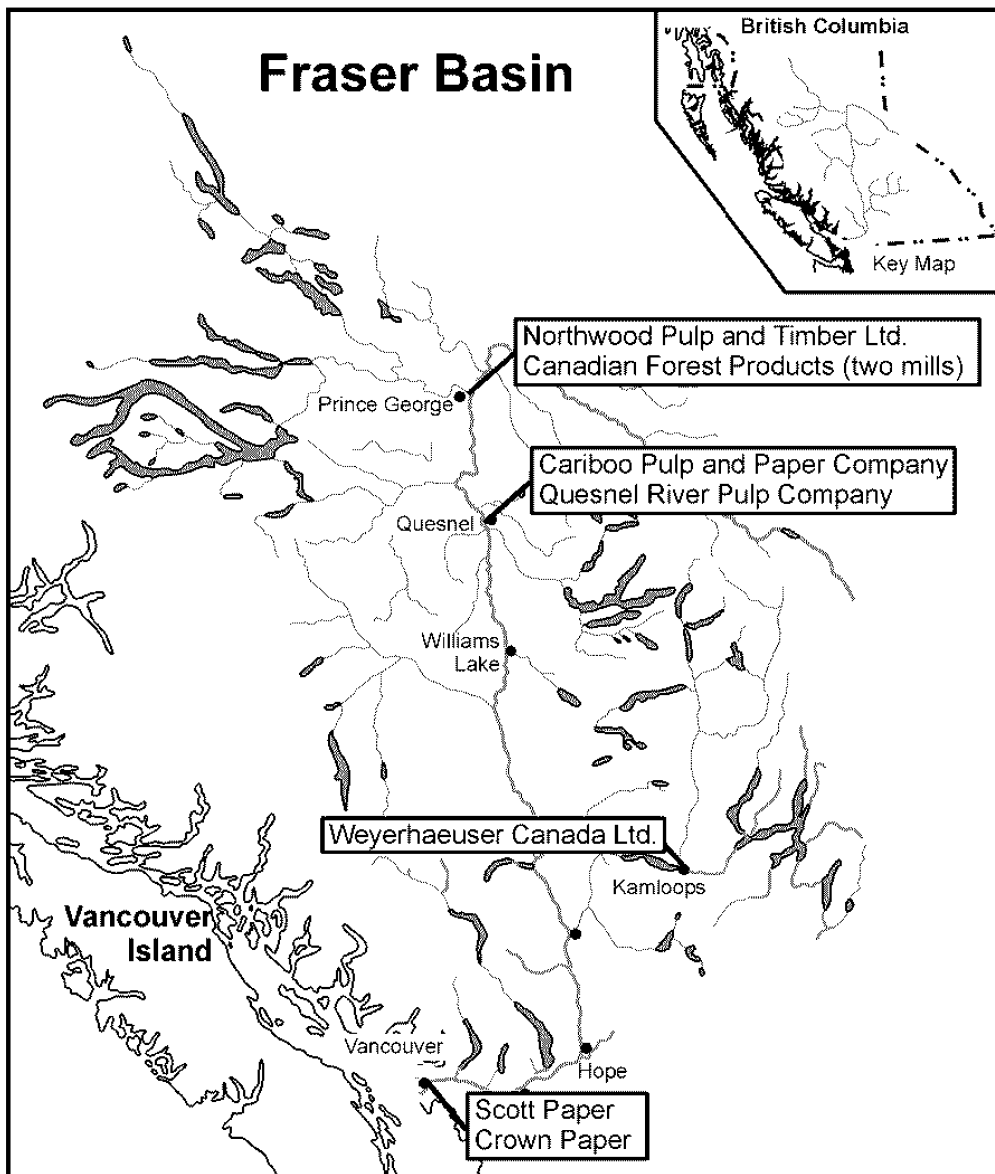
### ***3.2.2 Fraser River Estuary***

The Annacis Island, Lulu Island, and Iona Island WWTPs released roughly one million m<sup>3</sup>/day of effluent into the estuary and Strait of Georgia in 1995 (Figure 7). Annacis and Lulu Island WWTPs accounted for roughly 90% of the TSS discharged within the Fraser Basin in 1995. Since completion of secondary treatment facilities at the Annacis and Lulu Island plants in 1998, TSS was reduced by 70% and BOD by 85% (McGreer and Belzer 1999). Since secondary treatment removes more solids and the contaminants adsorbed onto those solids, it is expected that many of the “traditional” sewage contaminants would also be removed. This includes PCBs, dioxins, furans, organochlorine pesticides, some heavy metals (copper and zinc are noted by McGreer and Belzer (1999) to have been reduced), some PAHs, and other contaminants that are readily adsorbed to organic particles. Furthermore, secondary treatment increases chemical breakdown so more organic contaminants will be broken down into degradation products. However, water soluble contaminants such as many new pesticides, pharmaceutical products, and other rarely analysed substances would be unlikely to be affected. Also, as mentioned in section 3.2, secondary treatment produces toxic degradation products and sludge.



**Figure 5. Urban and agricultural land use in B.C. is highly concentrated in the lower Fraser Valley and coastal areas around the Strait of Georgia (Figure from Grant and Ross 2002 after modified sources: Geographic Data B.C. 2001 and Staubitz et al. 1997).**





**Figure 6. Major pulp and paper mills discharging to the Fraser River and estuary. Mill locations from: (B.C. Min. Env. Lands and Parks 2001).**



Figure 7. Major waste water treatment plants (WWTPs) in the Strait of Georgia and Puget Sound. Figure from: (Grant and Ross 2002 based on data from People for Puget Sound and Georgia Strait Alliance 1995).

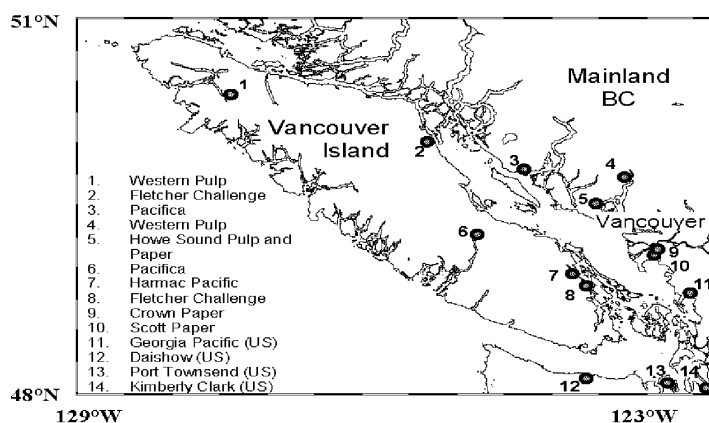


Figure 8. Pulp mills of Vancouver Island, Strait of Georgia and Juan de Fuca Strait. Figure from : (Grant and Ross 2002, mill locations from BC Min. Env. Lands and Parks 2001).



### **3.2.3 The Georgia Basin**

A number of municipal WWTPs discharge into the Georgia Basin (Figure 7). The two most significant are Clover Point and Macaulay Point which discharge only pre-treated sewage from the population centre of Victoria on southern Vancouver Island.

Debate has raged internationally on the topic of upgrading Victoria's treatment system. The main reason that little has been done to date is that some scientific work suggests that the strong tidal flows through the Juan de Fuca Strait allow significant dilution of the outflow such that environmental impacts are minimal (Taylor et al. 1998). However, widespread shellfish closures in the area are likely related to a combination of sewage effluent, agricultural runoff and leaking septic fields. Also, recent work has shown that despite tidal flows and dilution, the plumes from the discharge pipes rise to the ocean surface during eight months of the year (Steve Samis, personal comm., 2002). No information was found on more recent contaminants of concern such as pharmaceuticals, "New" POPs, and current pesticides, all of which are likely to be part of WWTP effluent and some of which may be unaffected by secondary treatment.

### **3.2.4 The Puget Sound Basin**

The Puget Sound Basin in Washington State has 26 major and 44 minor municipal sewage treatment plants (Figure 7). All of these plants currently employ secondary treatment (Grant and Ross 2002). No information was found on the possible influence of these discharges on the Strait of Georgia or the Strait of Juan de Fuca.

### **3.2.5 Summary**

By 1999, 55% of the municipal population of the Georgia Basin was served by sewage systems that had either secondary or tertiary treatment, representing a substantial increase from less than 20% prior to 1999 (Environment Canada 2001). This change likely improved some effluent quality characteristics such as BOD, TSS, and regulated contaminants such as heavy metals, some PAHs, PCBs etc. However, some sewage contaminants, particularly those of more recent concern, may either not be removed by secondary treatment or may be transformed into more toxic degradedates (e.g. alkylphenol ethoxylates discussed in section 12.2.2 and drugs and hormones discussed in section 10). Therefore, despite improved treatment, some toxic contaminants are likely released via WWTPs in concentrations that would increase with increasing human population size. This should not be interpreted to mean that secondary treatment is not worth while rather, it suggests that research is needed to determine whether the chemicals which survive secondary treatment are present in concentrations high enough to be of concern.

## **3.3 PULP AND PAPER MILLS**

There are 18 pulp mills B.C. Four of these 18 mills are too remote to have a consistent impact on the late-run sockeye population. Two mills (Skeena Cellulose and Eurocan) are located on the north coast of B.C. (and thus not shown in Figures 6 or 8) and two are located on the west coast of Vancouver Island (Western Pulp and Pacifica). Another four pulp mills in the U.S. are relevant to the habitat of Fraser River sockeye salmon habitat

(Figure 8).. Within the Strait of Georgia and Johnstone Strait, there are six B.C. mills that discharge into the marine environment (Figure 8) (Fletcher Challenge (2 mills), Pacifica Paper, Western Pulp, Howe Sound Pulp and Paper, and Harmac Pacific). A further six mills are located in the Fraser Basin above Hope (Figure 6) (Canfor (2 mills), Northwood, Cariboo Pulp, Quesnel River Pulp, and Weyerhaeuser) and two mills discharge into the Fraser estuary (Scott Paper and Crown Paper).

All of the B.C. pulp mills fall under federal legislation which does not allow the release of acutely toxic effluent and more recently has severely restricted allowable dioxin and furan releases. By 1993, all B.C. pulp and paper mills had full secondary effluent treatment, involving bacterial decomposition of organic matter, except for Scott Paper (Grant and Ross 2002). This effluent treatment and changes in chlorine use (largely a switch from Cl to ClO<sub>2</sub>) have resulted in significant reductions in the toxicity of pulp and paper mill effluent. The improvements observed in B.C. pulp mill effluent since 1990 are summarized below (McGreer and Belzer 1999):

- The average acute toxicity of the effluent improved from 50% fish survival in 65% effluent solution concentration to 100% survival in 100% effluent concentration over 96-hour exposures.
- The number of days toxic effluent was discharged decreased by 99%.
- BOD decreased by 88% and is below allowable limits.
- TSS decreased 34% and is well below allowable limits.
- A 1996 study showed a 98.4% compliance with requirements of the Chlorinated Dioxins and Furans Regulations of the federal Canadian Environmental Protection Act (CEPA). This has resulted in a decline of over 99% in the discharge of dioxins and furans.

Despite these significant improvements there are still concerns about contaminants in pulp mill effluent. The general toxicity test of the effluent is for acute toxicity only, and does not test for sublethal effects or chronic exposures. Furthermore, while a number of water quality parameters are improved by the changes and a number of well known contaminants are significantly removed, there are a large number of contaminants which are of more recent concern and their response to mill procedure changes is not well understood. Endocrine disruption is one of the major known sublethal effects of pulp mill effluent and may result from a combination of endocrine disrupting compounds (EDCs) in the effluent such as natural plant hormones, heavy metals, chlorinated compounds, and surfactants such as the alkylphenol ethoxylates (Hewitt and Servos 2001; Fox 2001; Yang and Randall 1996; Hodson et al. 1992; Kiparissis et al. 2001). Research has demonstrated a decline in the concentrations of a large number of EDCs after secondary treatment of the pulp mill effluent (Janz et al. 2001). However, the study did not analyse for the degradates of the chemicals tested. The overall endocrine disrupting nature of the effluent was therefore not comprehensively evaluated. Since many contaminants break down to produce toxic or endocrine disrupting compounds, it is possible for secondary treatment to reduce the concentration of some chemicals while increasing the concentration of a breakdown product which is as much, or more, of an endocrine disruptor as the measured parent compound. Finally, there are a number of natural plant hormones that are released from wood during pulp processing. It is not

known how changes to pulp mill processes in the early 1990s might have affected the release of these endocrine disrupting chemicals.

### ***3.3.1 Fraser Basin Upstream of Hope***

A recent study of sediments and water quality both upstream and downstream of the six pulp and paper mills discharging into the Fraser Basin north of Hope (Sekela et al. 1995) found the following:

- Chlorophenolics, PCBs, PAHs, pesticides, fatty and resinous acids and nitrogen generally did not exceed water and sediment quality guidelines though they generally did exceed background levels.
- Phosphorus regularly exceeded guidelines on the Fraser mainstem and is believed to be related to multiple sources including industrial, agricultural, and municipal inputs.
- Heavy metals exceeded guidelines but are thought to be at natural levels.
- A number of compounds, including PCBs, PAHs, and pesticides, were found upstream and downstream of the pulp mills. This strongly indicates atmospheric transport of many persistent chemicals into formerly pristine and currently undeveloped areas.

More recent studies suggest that PAHs are of current concern. Wilson et al. (2000) found that juvenile chinook salmon in the upper Fraser River which showed subtle toxic effects were most likely affected by PAHs rather than PCBs, dioxins, or furans. Yunker et al. (in press) note that the entire Fraser River basin shows levels of PAHs that exceed expected background levels. The source of these PAHs would include both the local point sources such as pulp mills and municipal waste water, and a variety of non-point sources described in the next section.

### ***3.3.2 Summary***

Process changes and increased effluent treatment have reduced the output of many contaminants from pulp and paper mills. This includes heavy metals, dioxins, furans, and a number of other chlorinated compounds, as well as water quality criteria such as BOD and TSS. However, a number of natural biological chemicals, such as resin acids and plant hormones and some chemicals added during pulp processing, are not being analysed in effluent sufficiently to determine the trend in their concentrations. There is evidence that some added chemicals, such as alkylphenol ethoxylates, may be degraded by the new processes into chemicals that are at least as toxic and/or endocrine disruptive. It is also possible that the process changes at pulp mills could result in an increase in natural plant hormone release. For these reasons, pulp and paper mills remain relevant to the late-run sockeye issue despite reductions in the release and/or production of some contaminants.



## 4 NON-POINT SOURCE POLLUTION

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### 4.1 URBAN RUNOFF

Urban centers generate large amounts of pollution. Some of this pollution is sent into the atmosphere, some into point source liquid effluent that is sometimes treated, and some into solids and liquids that are exposed to rainfall and become part of runoff. There are a number of reasons to suspect that the amount of urban runoff (and its pollutants) ending up in Fraser Basin waterways is increasing. Population size is increasing in the Fraser Valley, Vancouver, and other urban centres within the Fraser Basin. Most municipalities are converting existing combined sewer systems into separate sewer and stormwater systems. In most cases this means that stormwater will be discharged directly to the nearest stream/river without passing through a treatment facility. The increasing use of convenient lawn and garden products also contributes to the toxic runoff.

The most common chemicals detected in B.C. storm drains are heavy metals. Chromium, copper, lead, zinc, nickel and arsenic have been detected in stormwater outfalls along the Thompson River. In some cases high metal concentrations have been associated with stormwater from industrialized areas (Environment Canada 1997b) while other studies have shown that metals and vehicular traffic are related (Macdonald et al. 1997). Hall et al. (1999) show that contaminant loading increases proportionately with increases in vehicle traffic and with increases in the percentage of impervious surface area in the watershed (pavement, roofs etc.). Table 1 shows the estimated annual contaminant loading of a selection of contaminants from urban runoff in the Fraser Basin in 1992. These data show that hydrocarbons represent another major contaminant in urban runoff. More recent work by Yunker et al. (in press) shows heavy impacts of PAH contamination in urban areas largely attributable to vehicular emissions. Some of these PAHs reach the aquatic environment via runoff. Macdonald et al. (1992 and 1998) have investigated the input of PCBs, dioxins and furans to the B.C. aquatic environment. These inputs have largely been attributed to pulp mill effluent although Bright et al. (1999) found that more than 50% of the input of dioxins and furans in the Strait of Georgia can not be attributed to pulp mills and may be related to pentachlorophenol-based wood preservatives. Other contaminants that would reasonably be expected in urban runoff are atmospheric pollutants like POPs and PAHs, apparently ubiquitous contaminants like phthalate esters and poly-brominated diphenyl ethers (PBDEs).

Pesticides are also a concern in urban runoff. The National Water-Quality Assessment (NAWQA) program in the U.S. found pesticides in 95% of all streams sampled. Furthermore, 80% of urban streams contained five or more pesticides (United States Geological Survey 2001). A study conducted in the Puget Sound Basin found that, in general, urban streams contained more pesticides than agricultural streams (United States Geological Survey 2000; United States Geological Survey 1997). Diazinon was the most common pesticide found in these studies and has been targeted by some researchers as a possible cause of salmon stock decreases in the Pacific Northwest (Ewing 1999).

**Table 1: Estimated annual contaminant loading (in tonnes) from urban runoff in the Fraser Basin. Source: (McGreer and Belzer 1999 after Stanley Associates Engineering Ltd. 1992).**

Contaminant	Fraser Basin	Lower Fraser	Thompson	Middle Fraser	Upper Fraser
Suspended solids	62782	54584	1689	913	5596
Ammonia	75.3	65.5	2	1.1	6.7
Nitrate/nitrite	351.6	305.7	9.5	5.1	31.3
Total nitrogen	878.9	764.2	23.7	12.8	78.3
Total phosphorus	175.8	152.8	4.7	2.6	15.7
Lead	75.3	65.5	2	1.1	6.7
Copper	17.6	15.3	0.5	0.3	1.6
Zinc	75.3	65.5	2	1.1	6.7
Chromium	5	4.4	0.14	0.07	0.45
Cadmium	4	3.5	0.1	0.06	0.36
Nickel	12.6	10.9	0.3	0.18	1.1
Arsenic	6.5	5.7	0.2	0.1	0.6
Phenols	6.5	5.7	0.2	0.1	0.6
Total Hydrocarbons	2009	1747	54.1	29.2	179.1
PAHs	0.5	0.44	0.01	0.01	0.004

*Lower Fraser denotes the Fraser River watershed from Hope downstream. Thompson denotes the North and South Thompson and Thompson River watersheds. Middle Fraser denotes the Fraser River watershed from Hope to about the West Road River confluence with the Fraser. Upper Fraser denotes the watershed upstream of the West Road River.*

## 4.2 AGRICULTURAL RUNOFF

Agriculture in developed nations has become more and more intensified with time. The trend requires fewer farmers with less land to produce more product. This requires “enhancing” growing conditions for crops in the natural environment. The use of fertilizers and other chemicals has increased nine-fold worldwide between the late 1940s and late 1980s (Schreier et al. 1991 after Brown 1988). The Lower Fraser sub-basin applied 52% of all fertilizers used in the Fraser Basin in 1986, with the application rate (in kg/ha/year) being the highest in Canada. Surplus natural fertilizer also occurs due to a high livestock density. European countries have estimated roughly 2 to 2.3 grazing animals per hectare as being the highest allowable density before environmental affects ensue (Schreier et al. 1991 after Brown 1988). By 1986 the Lower Fraser sub-basin had already exceeded that number and in addition, contained 255 chickens per hectare and 2.1 pigs per hectare (Schreier et al. 1991). These data point to a major problem with nitrate and phosphate loadings to the environment. In addition, 1986 data showed that 90% of all insecticides and 56% of all herbicides used for agriculture in the province were applied in the Lower Fraser sub-basin (Schreier et al. 1991 based on hectares sprayed per year). Finally, modern farming practices often involve chemicals in feed that augment growth and development. These man-made chemicals and natural hormones end up in animal waste material that is then applied to cropland and through runoff may be transported into the Fraser River. Researchers in the U.S. are finding increasing evidence that runoff from cattle feedlots could be affecting local fish. Hormones in river water are part of the nation-wide survey of rivers and streams by the U.S. Geological Survey, but

these data are not expected to be released until 2003 (Renner 2002a). As of the Pre-1999 Annual Compliance Reports (Environment Canada 1998), agricultural practices in B.C. are under review but enforcement of “best practices” procedures had not yet begun. Contamination of the Fraser River by agricultural runoff is likely to be increasing due to the steady increase in agricultural intensity and chemical use in the Fraser Valley (more detail in section 6).

### **4.3 ATMOSPHERIC POLLUTION**

Atmospheric pollution dominantly comes from vehicular emissions, agricultural emissions, industrial emissions, and long-range transport from distant sources. The high population density and intense agricultural activity in B.C.’s Lower Mainland make it particularly susceptible to the first two sources.

Vehicular emissions include metals and a number of organic contaminants such as PAHs. Proximity to urban centres leads to increasing concentrations of metals associated with transportation, including zinc, copper and manganese (McGreer and Belzer 1999 after Belzer et al. 1998). Vehicular emissions will likely increase with increasing population numbers and increasing commuting time.

Agricultural emissions include chemicals from fertilizers, such as ammonia, as well as pesticides. Pesticides detected in air samples from Agassiz and Abbotsford (farming communities of the eastern Fraser Valley) in 1996 are shown in Table 2. Such chemicals can be removed from the air by either wet or dry precipitation and then make their way into the Fraser River. Increasing use of some pesticides will inevitably lead to higher concentrations in air and in the aquatic environment.

Long-Range Transport of Atmospheric Pollutants (LRTAP) has been the subject of much recent work. Studies have shown that a large number of chemicals are transported atmospherically across the globe in a fairly short time. The Arctic environment has become polluted with a number of POPs and other toxic substances initially explained by their volatilization in warmer climates and subsequent condensation in the colder arctic environment (Simonich and Hites 1995). The actual cause of this transport and concentration of contaminants is now thought to be the result of a number of physical and chemical processes (Macdonald et al. 2002). This concentration of contaminants has also been observed at higher elevations, with relatively high concentrations found in high altitude snow and lakes in the mountains of B.C. (Blais et al. 1998). Furthermore, the prevailing winds across the Pacific Ocean have been found to bring contaminants from Asia to North America within a matter of days (Wilkening et al. 2000; Strachan 1990). Many “legacy” POPs, including PCBs, are banned in North America, but are delivered through such processes to B.C. from regions where these chemicals are still being used, ensuring “fresh” inputs (Campbell et al. 2000). Some of the banned organochlorine contaminants do show a decline in sediments over the last 30 years (Macdonald et al. 1992).

**Table 2: Mean concentrations (ng/m<sup>3</sup>) of agricultural chemicals in ambient air samples collected weekly from January 1996 to December 1996.**  
**Source: (McGreer and Belzer 1999 after Belzer et al. 1998).**

<b>Pesticide Group</b>	<b>Chemical</b>	<b>Agassiz</b>	<b>Abbotsford</b>
Organochlorine	Aldrin	nd	0.246
Pesticides	Captan	1.448	1.823
	cis-Chlordane (a)	0.226	0.188
	trans-Chlordane (g)	0.260	0.102
	Dacthal	0.363	0.478
	4,4'-DDE	0.139	nd
	Dicofol	0.337	nd
	Dieldrin	1.010	0.062
	Endosulfan I	0.708	0.620
	Endosulfan II	0.253	0.184
	Heptachlor	0.148	1.024
	Heptachlor Epoxide	0.288	0.131
	Hexachlorobenzene	0.474	0.190
	Lindane (g-BHC)	0.338	0.213
	cis-Nonachlor	0.184	nd
	trans-Nonachlor	0.217	0.077
	Oxychlordane	0.278	0.244
Herbicides	2,4-D	6.646	2.301
	Dicamba	1.708	nd
	Dinoseb	nd	4.770
	Silvex (2,4,5-TP)	2.065	1.242
	Atrazine	5.529	2.622
Organophosphate	Chlorpyrifos	0.612	0.666
Pesticides	Diazinon	0.484	4.664
	Dichlorvos	2.990	1.172
	Dimethoate	0.340	nd
	Fonofos	0.957	0.128
	Malathion	1.963	3.688
	Mevinphos	nd	5.556
	Parathion Methyl	0.157	0.418
	Terbufos	0.512	1.246

*nd denotes not detected*



## 5 ENDOCRINE DISRUPTING CHEMICALS

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The term “Endocrine Disrupting Compound” (EDC) refers to a chemical’s ability to modify, mimic or generally disrupt natural hormonal processes. The healthy development and function of an organism is dependent on a highly regulated and complex interaction of hormones. This interaction involves three main systems: the immune system, the nervous system, and the endocrine (hormonal) system. The immune system is tasked with resisting infectious agents, foreign substances and foreign or damaged cells. The functioning of the immune system depends on chemical signalling provided by the endocrine system (Myers 2002b; Warhurst 1999). The nervous system deals with rapid communications in the body. The development of the nervous system can be affected by EDCs during early life stages (Myers 2002b; Warhurst 1999; Cooney 2000; Lister and Van der Kraak 2001). Furthermore, some EDCs can affect the signalling between nerves (Warhurst 1999; Lister and Van der Kraak 2001). The endocrine system itself is involved in the body’s chemical balance. Hormones generally act as long term messages (compared to the nervous system) and control development, affect behaviour, and are often involved in the timing of changes in the body. Table 3 illustrates the two main forms of cellular response to endocrine system controls, permanent developmental changes and transitory triggers.

The concern over EDCs in Canada has led to the devotion of a theme issue of the Water Quality Research Journal of Canada to this topic (volume 36, no. 2, 2001). Tables 3 through 7 originate from these summary articles. Table 4 lists the Canadian sites and sectors that are of greatest concern to endocrine disruption in fish. Municipal, pulp and paper, and agricultural effluents are the main areas of concern for the Fraser Basin. Table 5 lists some of the classes of chemicals associated with endocrine disruption that have been found in Canadian aquatic environments. Note that many of these substances are POPs, representing both “legacy” (largely regulated or banned in North America) and “new” (largely unregulated or still in use in North America). Table 6 lists the chemical constituents of complex mixtures (effluents etc.) that are known or suspected to have caused endocrine disruption in Canada. Table 7 lists the actual responses measured in aquatic organisms that are attributed to endocrine disruption in the Canadian environment. Finally, Tables 8 and 9 list the substances known or suspected to be endocrine disruptors according to the World Wildlife Fund (WWF) and the Pesticide Action Network Europe (PAN Europe).

Most of the chemical categories reviewed in this report are listed somewhere as either known or suspected endocrine disruptors.

***Due to a lack of data specific to sockeye habitat, the potential for EDCs to play a roll in the observed sockeye behaviour change cannot be adequately assessed. However, many EDCs are present in the B.C. aquatic environment and have the capacity to cause developmental and behavioural changes in fish.***

**Table 3:** A summary of cellular responses mediated by hormones acting through organizational or activational mechanisms. Source: (Lister and Van der Kraak 2001).

Cellular responses	
Organizational (developmental)	Activational (triggers)
Early in development	Throughout development
Irreversible	Reversible
Permanent	Transitory (homeostatic)

**Table 4:** Major Canadian sites and/or sectors of concern for potential endocrine disruption in fish. Source: (McMaster 2001 after Servos et al. 2000).

Site or sector identified
1. Municipal effluents
2. Intensive agriculture, including pesticides and livestock production
3. Textile mill effluents
4. Pulp and paper sector
5. Mining and metals
6. Historically contaminated sites, e.g., Sydney Tar Ponds
7. Identified Areas of Concern (AOCs), e.g., the Great Lakes
8. Contaminants in the Arctic, including aboriginal foods

**Table 5: Major chemical classes associated with endocrine disruption and their inputs to Canadian aquatic environment. Source: (Hewitt and Servos 2001).**

Class	Examples of specific chemicals	Inputs to Canadian aquatic environments
Industrial chemicals	PCBs + metabolites	<ul style="list-style-type: none"> <li>Industrialized harbours</li> <li>Atmospheric deposition</li> </ul>
	Non-ionic surfactants (APEOs)	<ul style="list-style-type: none"> <li>Municipal sewage effluents</li> <li>Textile effluents</li> <li>Industrial sites</li> </ul>
	Brominated diphenyl ether	<ul style="list-style-type: none"> <li>Industrialized harbours</li> <li>Flame retardant leachates</li> </ul>
	Phthalates	<ul style="list-style-type: none"> <li>Plastic leachates</li> </ul>
	Bisphenol A	<ul style="list-style-type: none"> <li>Municipal sewage</li> <li>Industrialized harbours</li> </ul>
Pesticides	Organochlorines (eg., DDT)	<ul style="list-style-type: none"> <li>Atmospheric deposition</li> <li>Agricultural runoff</li> </ul>
Halogenated organic contaminants	TBT	<ul style="list-style-type: none"> <li>Marine harbours</li> <li>Application sites</li> </ul>
	PCDD/PCDFs	<ul style="list-style-type: none"> <li>Industrialized harbours</li> <li>Wood preservatives</li> <li>Contaminated sediments</li> </ul>
Other pollutants	Heavy metals	<ul style="list-style-type: none"> <li>Acid rain</li> <li>Chlor-alkali plants</li> <li>Mine tailings</li> </ul>
	PAHs	<ul style="list-style-type: none"> <li>Industrialized harbours</li> <li>Atmospheric deposition</li> <li>Oil sands deposits and processing</li> </ul>
Natural products	17 $\beta$ -estradiol	<ul style="list-style-type: none"> <li>Municipal sewage</li> <li>Animal waste runoff</li> </ul>
	Plant sterols Stillbenes Flavinoids	<ul style="list-style-type: none"> <li>Pulp mill effluents</li> <li>Agricultural runoff</li> </ul>

**Table 6:** Complex mixtures in Canadian aquatic environments known or suspected to have the potential to affect endocrine function in aquatic biota. Source: (Hewitt and Servos 2001).

Complex Mixture	Potentially associated chemicals
Pulp and paper mill effluents	Natural wood derivatives PCDD / PCDFs Plant sterols
Municipal effluents and urban runoff	APEOs Endogenous and synthetic hormones Bisphenol A PAHs
Textile mill effluents	APEOs
Contaminated sediments	PAHs PCBs PCDD / PCDFs Heavy metals
Agricultural runoff	Pesticides Endogenous hormones Phytoestrogen metabolites

**Table 7: Endocrine-related responses identified in fish and other aquatic organisms within the Canadian environment. Source: (McMaster 2001).**

Source, sector, location or species	Identified compounds	Response measured	Endocrine disruption?
Great Lakes salmonids	TCDD and related compounds Unknown	Larval mortality Thyroid abnormalities	Potential Potential
Pulp and paper mill effluent	Unknown	Altered reproductive function	Yes
Municipal wastes	Estradiol, estrone and ethinylestradiol	Vitellogenin induction	Potential
	Unknown	Immune stimulation	Potential
Heavy metals	Zinc, copper, cadmium, iron	Altered adrenal function	Yes
Pesticides, insecticides and agricultural runoff	4-NP	Altered smoltification	Yes
	Equol, estradiol	Endocrine active compounds present	Potential
	Unknown	Reproduction and growth	Potential
Refinery discharges and steel mill effluents	Estradiol, estrone and ethinylestradiol	Vitellogenin induction	Potential
	PAHs	Immune modulation	Potential
		Sex steroids	Potential
Tributyltin	TBT	Imposex	Yes

**Table 8: WWF list of endocrine disrupting pesticides with additions from the PAN Europe list. Source: (Schmitt 2000 and World Wildlife Fund Canada 1999 after Colborn et al. 1993).**

<b>Insecticides</b>	<b>Herbicides</b>	<b>Fungicides cont.</b>
Aldrin	2,4-D	Metiram
Befenthrin	2,4,5-T	Triadimefon
Carbaryl	Acetochlor	Tributyl-tin
Carbofuran	Glufosinate-ammonium	Vinclozolin
Chlordane	Alachlor	Nabam
Chlordecone	Amitrole	Zineb
Chlorfentezine	Bromacil	Ziram
1-cyhalothrin	Bromoxynil	
Deltamethrin	Cyanazine	
DDT and metabolites	DCPA	<b>Other Pesticides</b>
DBCP	Ethiozin	Ethylene thiourea (ETU)
Dicofol	Atrazine	Pentachlorobenzene
Dieldrin	Ioxynil	Pentachlorophenol (PCP)
Dimethoate	Linuron	Piperonyl butoxide
Dinitrophenol	Metribuzin	
Endosulfan ( $\alpha$ and $\beta$ )	Molinate	<b>PAN Pesticides</b>
Ethofenprox	Nitrofen	Amitraz
Fenitrothion	Oryzalin	Carbendazim
Fenvalerate	Paraquat	Chlorpyrifos
Fipronil	Oxyacetamide	Demeton-s-methyl
$\beta$ -HCH	Trifluralin	Dichlorvos
toxaphene	Picloram	Epoxyconazole
Heptachlor	Pendimethalin	Fentin acetate
H-epoxide	Prodiamine	Glyphosate
Endrin	Pronamide	Metam sodium
Lindane ( $\gamma$ -HCH)	Simazine	Oxydemeton-methyl
Malathion	Terbutryn	Penconazole
Methomyl	Thiazopyr	Prochloraz
Methoxychlor	Triclorobenzene	Procymidone
Mirex		Prometryn
Oxychlordane	<b>Fungicides</b>	Propiconazole
Parathion	Benomyl	Thiram
Photomirex	Etridiazole	Triphenyltin
Pyrethrins	Fenarimol	Trichlorfon
Synthetic pyrethroids	Fenbuconazole	Tridemorph
Ronnel (fenchlorfos)	Hexachlorobenzene	
Aldicarb	Mancozeb	
trans-nonachlor	Maneb	
n-2-fluorenylacetamide	pentachloronitrobenzene	

**Table 9: Industrial chemicals from the WWF list of endocrine disrupting substances. Source: (World Wildlife Fund Canada 1999 after Colborn et al. 1993).**

Industrial Chemicals	
4-OH-alkylphenol	3-OH 2',3',4',5' tetrachlorobiphenyl
Aluminum	4-OH 2',3',4',5' tetrachlorobiphenyl
Benzopyrene	2,2',3,3',6,6' hexachlorobiphenyl
Bisphenol-A	Pentabromodiphenyl ether
4-OH-biphenyl	Penta- to nonylphenols
t-butylhydroxyanisole (BHA)	Phthalates
Cadmium	Benzylbutylphthalate
Carbon disulfide	di-2-ethylhexylphthalate (DEHP)
Dioxin (2,3,7,8-TCDD)	Diisobutylphthalate
Furans	di- <i>n</i> -hexylphthalate (DnHP)
Hydroxy (hydro)-quinones	di- <i>n</i> -octylphthalate (DnOP)
Lead	di-OH-benzoicacids (DHBA)
Mercury	Phenol
Methylcolanthrene (MCA)	Polychlorinated diphenyl ether
Polybrominated biphenyls (PBBs)	Radioactive iodine
Polychlorinated biphenyls (PCBs)	Resorcinol
2 to 4-OH 2',5' dichlorobiphenyl	Styrenes
2,3,4 trichlorobiphenyl	Tetrachloro-benzyltoluenes
4-OH trichlorobiphenyls (2,2',5; 2',4',6')	Thiocyanate
	Vinyl acetate





## 6 PESTICIDES

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### 6.1 BACKGROUND

The dependence of industrialized nations on high intensity agriculture has led to the use of specialized chemical protection to increase crop yield. The three main categories of agricultural pesticides are insecticides, herbicides, and fungicides. The extensive use of each of these pesticides has reduced farm labour and increased crop productivity. The variety of pesticides available and their volume of use expanded following World War II (Smith 1987). Organochlorine (OC) pesticides were the first class to reach significant levels of use. The discovery that these chemicals are persistent, are bioaccumulative in food chains, and can affect entire populations of wildlife and humans led to restrictions and bans on their use. The need for agricultural production to support a growing human population meant that where one group of pesticides could not be used, others were designed to take their place. Organophosphate (OP) and carbamate pesticides gained in importance from the 1950s onwards to replace the OC pesticides (Murty 1986a). The newer OP and carbamate compounds are generally not as persistent or as bioaccumulative as the older OC pesticides. However, they are among the most acutely toxic of all pesticides to vertebrate animals (Pan-uk 1996). Direct mortality of fish and wildlife are far more often documented for OP and carbamate pesticides than for OC pesticides (Glaser 2001 after Hayes and Wayland 1975; Glaser 2001 after Grue et al. 1983). Despite their low persistence, studies have shown that in regions of pesticide use, the effects of the pesticide can be detected in non-target aquatic biota for a period of several months (Gruber and Munn 1998). Most of the OP and carbamate pesticides work by AChE inhibition.

A wide variety of other chemical groups are also used as pesticides in British Columbia. Pesticide use has expanded beyond that of agriculture. Recent data show that the urban use of pesticides significantly exceeds that of agricultural use in the Puget Sound Basin (Grant and Ross 2002 after Tetra Tech Incorporated 1988).

### 6.2 SOURCES

Pesticide pollution can be from both point sources and non-point sources. Point source pesticide pollution originates from spills, improper disposal, or when pesticides become part of an effluent stream, such as storm drains, sewage outfalls, or industrial effluent. However, the broad application of pesticides to crops, lawns and forests results in dominantly non-point source pollution in the form of runoff. Pesticides can also get into surface waters from overspraying, from erosion of contaminated soils, and from contaminated groundwater.

Pesticides have been detected at very high levels in B.C. agricultural drainage ditches (Wan et al. 1994). Researchers in the U.S. found that an application of diazinon to two yards in a neighbourhood resulted in detectable levels in the nearby stream within days (Ewing 1999). This non-point source pollution from many areas can result in relatively constant levels of contamination. As part of the NAWQA program the U.S. Geological Survey led a nation wide study of pesticides in major rivers (United States Geological Survey 2001). The study found that 95% of rivers had at least one detectable pesticide.

This suggests that pesticide pollution is not infrequent and variable but is ubiquitous, particularly in water bodies near urbanization or heavy agricultural use. The lower Fraser River possesses both of these attributes (Figure 5).

Many pesticides can also volatilize and become airborne pollutants that later precipitate. This has been confirmed by studies that have detected pesticides in air, rainfall, snow, and fog (Simcik et al. 2000; Rawn and Muir 1999; Chernyak et al. 1996; Rice and Chernyak 1997; Eisenreich et al. 1989; Strachan 1990).

### **6.3 B.C. PESTICIDES**

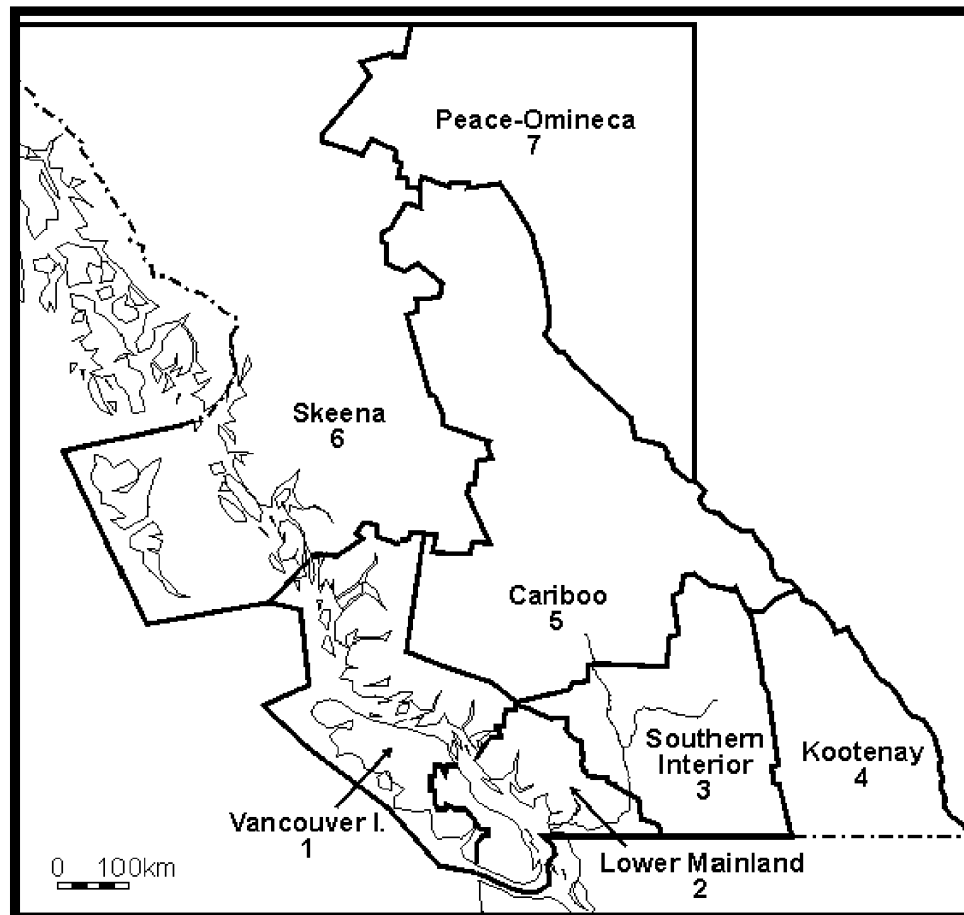
In 1991, 1995, and 1999 Environment Canada and the B.C. Ministry of Environment, Lands and Parks (B.C. MELP) contracted out surveys of pesticide sales in B.C. By repeating the survey three times, the consultant (ENKON Environmental Limited 2001) made it possible to plot the change in pesticide sales through time with three data points. This is ideal for use with this study since our main assumption for prioritizing contaminants is that they be either new or increasing during the same period as the sockeye behaviour change. The ENKON study included sales of reportable pesticides (Restricted and Commercial labels) and a survey of wood preservative and anti-sapstain chemical use (these two categories will be discussed in detail in sections 7 and 8). The study also looked at pesticide use by licensed agricultural and landscape services in the Lower Mainland only (Area 2, Figure 9).

There are two significant gaps in the pesticide survey data that must be recognized. First, the survey does not include domestic label products. Studies by the U.S. Geological Survey (discussed above) demonstrated that domestic pesticide use in urban areas is sufficient to deliver significant concentrations to surface waters and so the lack of domestic label data represents a significant knowledge gap. The sales data also only cover products sold within B.C. Two examples were found where there is evidence of heavy and increasing use of a pesticide which is not reflected in the sales data (metam sodium discussed below and triclopyr; discussed in section 9.1). Despite this, these surveys represent an excellent opportunity to observe changes in the volume of pesticide sales in British Columbia through the 1990s.

The following points are based on the findings of the 1999 pesticide sales survey:

- Despite increasing awareness and adoption of Integrated Pest Management procedures, the total volume of reportable pesticide sales increased by about 19% from 1991 to 1999.
- In 1999, 8,102,384 kg of pesticide active ingredients (not including most domestic label products) were purchased or used in B.C. 86.5% of this total is accounted for by wood preservatives and anti-sapstain chemicals. In fact, 66.4% of the total is due to creosote and 11.4% is due to chromated copper arsenate (CCA). Both of these chemicals have increased significantly in use over the study period. The top 11 active ingredients account for 92.3% of ingredients used in 1999 (Figure 10).

- Approximately 80% of wood preservative use and 85% of reportable pesticide sales took place in the Lower Mainland and Southern Interior (Areas 2 and 3, Figure 9).
- Of the 277 reportable pesticide active ingredients, 166 showed an increase during the study period.



**Figure 9.** Map of the regions used for the 1999 pesticide sales survey. Figure source: (modified from ENKON Environmental Limited 2001).

## 6.4 ANALYSIS OF THE B.C. PESTICIDE SURVEY DATA

### 6.4.1 Prioritization Method

Since pesticides are by definition “toxic”, those used in B.C. during the 1990s could be potentially involved in the sockeye behaviour change. However, a limited list of more likely (higher priority) pesticide active ingredients can be made by discounting those pesticides which do not fulfill the following criteria (these criteria are based on the exposure scenarios discussed in section 1.4):

1. Pesticides whose sales did not increase from 1991-1995 and again from 1995-1999 are unlikely to have been involved in a behaviour change that appeared during this period and worsened over time.
2. Pesticides whose sales did not increase by at least 100 kg from 1991-1999 are unlikely to have reached the Fraser River in significant quantities.
3. Pesticides not sold extensively in Region 2 (Figure 9) are not likely to end up in the Fraser River (Region 3 was excluded as those pesticides used heavily there are related to fruit crops which are dominantly used in the Okanagan Valley and thus are unlikely to end up in the Fraser River.)
4. Pesticides showing no sales in 1995 or 1999 are unlikely to have been involved in the behaviour change.

Table 10 is formed by excluding all those pesticides which do not fit these criteria. Figure 11 illustrates graphically the change in use for a few of the higher sales pesticide ingredients. The graph includes bars indicating the percentage pre-spawning mortality of the late-run sockeye. It is not reasonable to make a detailed comparison of the pesticides with mortality since the pesticide data only has three points over 9 years versus the yearly data for the mortality. However, it is clear that a possible explanation for the mortality is that around 1995 one or a combination of these ingredients may have passed a concentration threshold beyond which the sockeye began to show a sublethal response.

Another difficulty in analysing this data is that they are records of sales and thus they may not necessarily correlate with use, nor with the likelihood of the chemical reaching the Fraser River. An example of this is the sales record of metam (Figure 11) which shows a dip in sales in 1995 and thus was excluded from the list of higher risk pesticides in Table 10. However, data for the agricultural application of metam in Region 2 shows that in 1999 its application actually exceeded its sales (Figure 11 and Table 11). The dramatic increase in use of metam by agriculture makes it a good candidate for the higher priority list. Table 11 shows this and seven other pesticide active ingredients that were excluded for the reasons relating to the sales data shown in the upper part of the table (in grey) but because of the agricultural application data (lower part of the table) they have been re-introduced to the list of higher risk pesticides. The uncertainties involved in this example illustrate that the next critical step in the investigation of the sockeye behaviour change is to obtain data on the chemicals actually present in the Fraser River and within sockeye fish tissues.

We then ranked our higher priority pesticides (Table 12) by using three simple criteria:

- The first criterion is 'total volume of sales in 1999' and is given the highest weighting:

- 1 point for sales of 100-1,000 kg
- 2 points for sales of 1,000-5,000 kg
- 3 points for sales of 5,000-10,000 kg and
- 4 points for sales of >10,000 kg

The assignment of these points is based on the assumption that a chemical is unlikely to be involved in the observed behaviour change unless significant amounts of it were used and thus could possibly reach sockeye habitat.

- The second criterion is the 'pattern of sales increase' and is based on the assumption that pesticides which showed a significant increase in 1995, or in both 1995 and 1999, are more likely to be involved:
  - 0 points for sales which either decreased from 1991 to 1995 or from 1995 to 1999
  - 1 point for sales which increased significantly from 1991 to 1995 or from 1995 to 1999, but did not increase significantly over both periods
  - 2 points for sales which increased significantly both from 1991 to 1995 and from 1995 to 1999
- The third criterion is 'degree of sales increase' and is based on the assumption that a more rapid overall increase (1991 to 1999) indicates a more likely chemical:
  - 0 points for increases of less than 100%
  - 1 point for increases from 100 to 1000%
  - 2 points for increases of >1000%

For example, formaldehyde scores four points for having 1999 sales of more than 10,000 kg (column 4 of Table 10), two points for having increased significantly over both 1991-1995 and 1995 to 1999 (columns 5 and 6 or 8 and 9 of Table 10), and 1 point for an overall degree of increase of between 100 and 1000% from 1991-1999. Note that the pesticide active ingredients added back in (in grey, Table 12), were subjectively scored on the second criteria as there was no agricultural use data for 1995. The score is based on an assessment of the significance of the agricultural use data compared to the sales data.

#### 6.4.2 *Prioritization Caveats*

It is recognized that these criteria are subjective, particularly where data was lacking and assumptions are made (e.g. metam sodium) but they are simply intended to provide some guide as to a means of ranking in a data poor situation.

The prioritization does not take into account lipophilic vs. hydrophilic properties because there are mechanisms by which both of these types of contaminants could be the cause of the sockeye behaviour; there is therefore little reason to show preference for one or the other. Persistence was not included for three reasons. First, because it is possible that the sockeye could experience a very short exposure and so the compound need not be persistent. Second, a large number of low persistence chemicals are released steadily to the environment creating a constant environmental exposure despite their rapid breakdown (Daughton and Ternes 1999). Third, persistence information is usually highly

variable since environmental conditions (e.g. temperature) greatly affect how long a chemical will persist. For example, glyphosate was found to oxidize in 3 days in Texas but lasted for a year in Canada (Ewing 1999). Additional details found for some of the pesticides are listed in the Selected Pesticide Notes in Appendix 1.

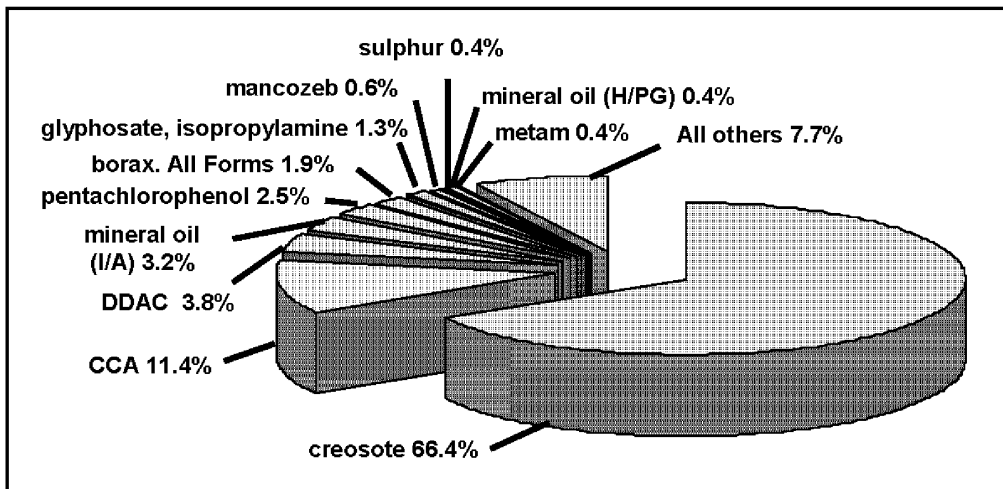


Figure 10. Relative sales (by weight) of the top 11 pesticides in 1999 which account for 92.3% of all ingredients sold. The wood preservatives creosote and CCA and the antisapstain chemicals DDAC and borax are discussed in sections 7 and 8. Data source: (ENKON Environmental Limited 2001).

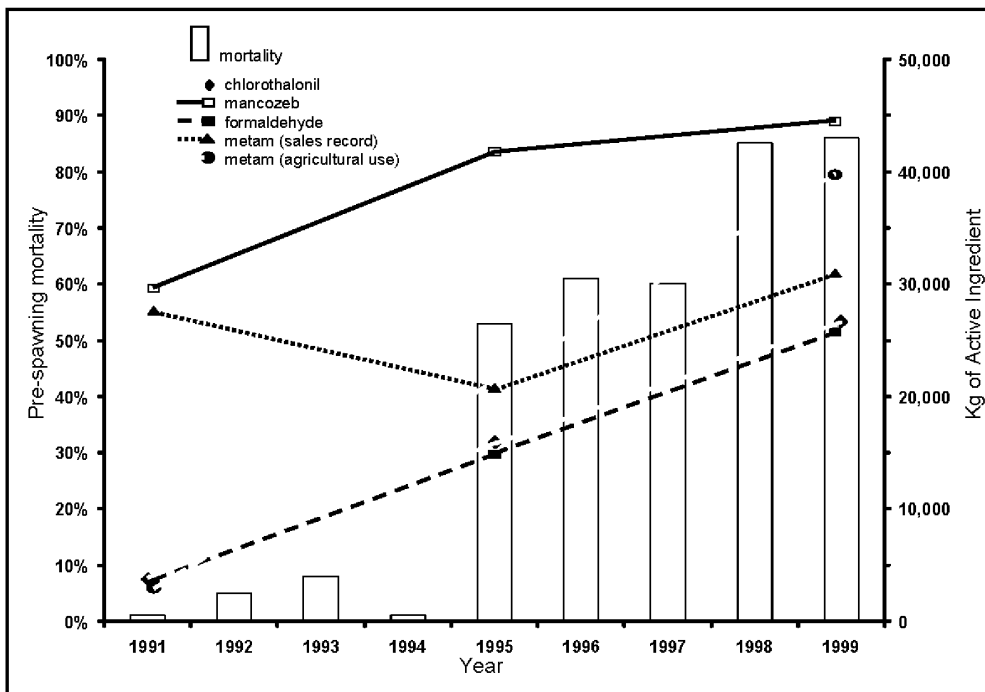


Figure 11. Graph of select pesticides showing increasing sales during the 1990s. With three data points it is not possible to look for close temporal correlation with pre-spawning mortality of late-run sockeye salmon. Data Source: (ENKON Environmental Limited 2001 and Lapointe 2002).

**Table 10: List of pesticide active ingredients from B.C. pesticide sales survey after elimination of candidates that scored poorly in our ranking scheme. Based on sales data from: (ENKON Environmental Limited 2001).**

Active Ingredient	Total Sales (kg)			Change in Sales (%)			Change in Sales (kg)		
	1991	1995	1999	1991-95	1995-99	1991-99	1991-95	1995-99	1991-99
chlorothalonil	3,721	15,871	26,640	327%	68%	616%	12,150	10,769	22,919
formaldehyde	3,007	14,342	25,495	377%	78%	748%	11,335	11,153	22,488
<i>Bacillus thuringiensis</i> , serotype H-14	3,188	11,270	21,875	254%	94%	586%	8,082	10,605	18,687
mancozeb	29,511	41,907	44,682	42%	7%	51%	12,396	2,775	15,171
<i>Bacillus thuringiensis</i> , Berliner ssp. Kurstaki	3,095	12,283	17,895	297%	46%	478%	9,188	5,612	14,800
dazomet	3,450	5,370	10,035	56%	87%	191%	1,920	4,665	6,585
cupric hydroxide	634	6,023	6,920	850%	15%	991%	5,389	897	6,286
diazinon	19,643	22,552	24,563	15%	9%	25%	2,909	2,011	4,920
iprodione	1,204	3,320	5,477	176%	65%	355%	2,116	2,157	4,273
Nonylphenoxypolyethoxyethanol	5,585	8,929	9,245	60%	4%	66%	3,344	316	3,660
Napropamide	3,666	5,102	6,693	39%	31%	83%	1,436	1,591	3,027
soap (insecticidal)	1,033	2,405	3,599	133%	50%	248%	1,372	1,194	2,566
metalaxyl	982	1,704	3,463	74%	103%	253%	722	1,759	2,481
terbufos	143	585	2,405	309%	311%	1582%	442	1,820	2,262
2,4-D Amine	12,327	12,340	13,903	0%	13%	13%	13	1,563	1,576
Chlormequat	833	997	1,388	20%	39%	67%	164	391	555
maelic hydrazide	2,576	2,672	3,126	4%	17%	21%	96	454	550
acephate	804	949	1,347	18%	42%	68%	145	398	543
Vinclozolin	0	56	528	na	843%	na	56	472	528
Propiconazole	18	40	508	122%	1170%	2722%	22	468	490
Dodemorph-acetate	55	320	480	482%	50%	773%	265	160	425
Permethrin	198	405	579	105%	43%	192%	207	174	381
Oxadiazon	0	254	299	na	18%	na	254	45	299
o-benzyl-p-chlorophenol	31	41	143	32%	249%	361%	10	102	112



**Table 11: Active ingredients reintroduced into our priority list as a result of evidence of heavy agricultural application data, despite reductions shown by reportable pesticide sales data. Based on sales and agricultural use data from: (ENKON Environmental Limited 2001).**

Active Ingredient	Total Sales (kg)			Change in Sales (%)			Change in Sales (kg)		
	1991	1995	1999	1991-95	1995-99	1991-99	1991-95	1995-99	1991-99
Paraquat	0	0	4,817	na	na	na	0	4,817	4,817
metam (metam sodium)	27,437	20,422	30,855	-26%	51%	12%	-7,015	10,433	3,418
Linuron	1,990	3,900	3,533	96%	-9%	78%	1,910	-367	1,543
Mecoprop amine	2,882	4,290	3,533	49%	-18%	23%	1,408	-757	651
Diquat	1,374	1,837	1,641	34%	-11%	19%	463	-196	267
Bentazon	1,433	1,377	1,314	-4%	-5%	-8%	-56	-63	-119
Chloropicrin	203	0	0	-100%	na	-100%	-203	0	-203
paraffin base mineral oil (adjuvant)	7,599	5,912	7,266	-22%	23%	-4%	-1,687	1,354	-333
Agricultural Application (kg)				Change in Application (%)			Change in Application (kg)		
	1991		1999	1991-99			1991-99		
Paraquat	23		164	613%			141		
metam (metam sodium)	2,124		39,854	1776%			37,730		
Linuron	0		531	na			531		
Mecoprop amine	247		580	135%			333		
Diquat	39		155	297%			116		
Bentazon	195		483	148%			288		
Chloropicrin	1,116		3,039	172%			1,923		
paraffin base mineral oil (adjuvant)	887		2,035	129%			1,148		

The top portion of this table shows reported B.C. sales and the listed ingredients were deemed poor candidates because of the data shaded in grey. The lower portion of this table shows agricultural application data for 1991 and 1999 which makes these ingredients candidates for the high risk list again.

**Table 12: Our prioritized list of pesticide active ingredients of concern in the context of the late-run sockeye crisis. Prioritization based on pesticide sales and use data from: (ENKON Environmental Limited 2001).**

Active Ingredient	Total Volume of Sales	Pattern of Sales Increase	Degree of Sales Increase	Final Score
metam (metam sodium)	4	2	1	7
Formaldehyde	4	2	1	7
Chlorothalonil	4	2	1	7
<i>Bacillus thuringiensis</i> , serotype H-14	4	2	1	7
dazomet	3	2	1	6
<i>Bacillus thuringiensis</i> , Berliner ssp. Kurstaki	3	2	1	6
Paraquat	2	2	2	6
Terbufos	2	2	2	6
Mancozeb	4	1	0	5
Diazinon	4	1	0	5
cupric hydroxide	3	1	1	5
Napropamide	3	2	0	5
Iprodione	2	2	1	5
Metalaxyl	2	2	1	5
soap (insecticidal)	2	2	1	5
2,4-D Amine	3	1	0	4
Nonylphenoxypolyethoxyethanol	3	1	0	4
linuron	2	1	1	4
Acephate	2	2	0	4
Chlormequat	2	2	0	4
Vinclozolin	1	2	1	4
Permethrin	1	2	1	4
Propiconazole	1	1	2	4
paraffin base mineral oil (adjuvant)	2	1	0	3
Chloropicrin	2		1	3
Mecoprop amine	2	1	0	3
Bentazon	2	1	0	3
dodemorph-acetate	1	1	1	3
Oxadiazon	1	1	1	3
o-benzyl-p-chlorophenol	1	1	1	3
maelic hydrazide	2	0	0	2
diquat	2	0	0	2

*Ingredients shaded in grey were re-introduced to the higher risk list due to agricultural application data. 'Total Volume of Sales': 1-4 points awarded for sales of 100-1,000 kg, 1,000-5,000 kg, 5,000-10,000 kg and >10,000 kg respectively.*

*'Pattern of Sales Increase': 0-2 points awarded for sales which decreased either from 1991-1995 or 1995-1999, sales which did not increase significantly over both periods, and sales which did increase significantly over both periods respectively.*

*'Degree of Sales Increase': 0-2 points awarded for a sales increase from 1991-1999 of less than 100%, 100%-1000%, and >1000% respectively.*

## 6.5 INERT PESTICIDE INGREDIENTS

The active ingredient in a pesticide is the ingredient that has been designed to perform the pesticidal activity. Inert ingredients (also called adjuvants) are chemicals added to a pesticide active ingredient to enhance the product. Some of these ingredients improve performance (synergists increase toxicity of other chemicals), ease application, improve pesticide solubility, allow the pesticide to spread over a surface or stick to leaves and soil (surfactant), improve the absorbability of the pesticide by insects, and increase product shelf life (National Pesticide Telecommunications Network 2000; United States Environmental Protection Agency 1996b).

Inert ingredients are considered part of the trade secret formulation of a pesticide and so do not have to be reported. The problem is that the term inert only means that the manufacturer did not define it as the active ingredient so the inert ingredient may be highly toxic, and perhaps even more toxic than the active ingredient (Northwest Coalition for Alternatives to Pesticides 1998). At least 394 chemicals that are used as inert ingredients in some pesticides have been used as active ingredients in others. The Northwest Coalition for Alternatives to Pesticides (NCAP) produced a report that lists the restricted use pesticides which have been used as inert ingredients including piperonyl butoxide, cuprous oxide, hydrogen cyanimide, chlorothalonil, and chloropicrin (Northwest Coalition for Alternatives to Pesticides 1998). Nonylphenol and the related ethoxylates are commonly used inert ingredients for their surfactant capability (Cox 1996). A number of researchers have looked at the toxicity of inert ingredients (Garry et al. 1999; McLeese et al. 1980; Anastacio et al. 2000; Lewis 1992; Lewis 1991; Fairchild et al. 1999). In many cases the inert ingredients were found to have significant toxicity, to increase the toxicity of the active ingredient, or to have other sublethal effects such as endocrine disruption.

The U.S. Environmental Protection Agency (EPA) has attempted to address this problem by creating five lists of inert ingredients (Northwest Coalition for Alternatives to Pesticides 1998; United States Environmental Protection Agency 2001a):

- List 1: Inerts of Toxicological Concern;
- List 2: Potentially Toxic Inerts (High Priority for Testing);
- List 3: Inerts of Unknown Toxicity;
- List 4A: Minimal Risk Inerts;
- List 4B: Inerts for which the EPA has sufficient information to conclude that their current use patterns will not adversely affect public health or the environment.

The EPA has encouraged pesticide producers to use only List 3 and 4 inerts and has required that List 1 inerts be mentioned on the label. This process has had mixed success. List 1 has shrunk from 57 ingredients to eight which indicates that 49 former List 1 ingredients are no longer being used as inerts in the U.S. However, List 2 inerts have grown from 67 to 101 and List 3 from roughly 800 to 1,981 chemicals between 1987 and 1995 (Northwest Coalition for Alternatives to Pesticides 1998). This process illustrates once again the tendency for industry to replace one regulated or restricted chemical with 2 or more new ones for which

little toxicity data exist. The USEPA List 1 includes dioctyl phthalate, formaldehyde, hydroquinone, isophorone, nonylphenol, phenol, and rhodamine B (United States Environmental Protection Agency 2001a).

It is most likely that as the overall use of pesticides in B.C. increases, the quantity of inert ingredients also increases. However, without information on which ingredients are being used and data on their toxicity, it is impossible to assess the potential impact of these chemicals.

## **6.6 PESTICIDE DEGRADATION PRODUCTS**

In most cases, little or no information exists about degradation products of pesticides. Alkylphenol ethoxylates degrade to substances that are more toxic and at least as endocrine disrupting as the parent compounds (Cox 1996). Metam sodium and dazomet are not highly toxic but both break down rapidly into methyl isothiocyanate (MITC) which is highly toxic to fish and is considered persistent (United States Environmental Protection Agency 2001b). As with the inert ingredients, the lack of information precludes the assessment of pesticide degradation products as a potential cause of the recent sockeye behaviour change.

*No data were found for concentrations of pesticides in the Fraser River or in sockeye salmon tissues. Data were available on sales of pesticides in B.C. for 1991, 1995, and 1999 and these data show an overall increase in pesticide use. We reduced the number of pesticides on this list and prioritized chemicals using assumptions based on the circumstances of the sockeye behaviour change. Little information currently exists on pesticide inert ingredients and degradation products, some of which are known to be highly toxic. The increasing use of pesticides in the Fraser Basin during the 1990s underscores the potential contribution of this category of contaminants to the sockeye salmon behaviour change, should contaminants be involved.*

## 7 WOOD PRESERVATIVES

Wood preservative use was included in the Survey of Pesticide Use in British Columbia: 1999 (ENKON Environmental Limited 2001). Only four wood preservatives were used in B.C. in 1999 and the data are summarized in Table 13. The survey notes that the majority of wood preservation facilities used only chromated copper arsenate (CCA). However, the three plants that applied creosote used enough to make creosote the most used pesticide in the province, alone accounting for 66.5% of all pesticides sold or used in B.C. in 1999 (by weight). 93% of wood preservative use in B.C. took place within the Lower Mainland, Southern Interior, and Cariboo regions (Regions 2, 3, and 5 in Figure 9) which cover slightly more than the Fraser River Basin.

Table 13 clearly shows a decrease in pentachlorophenol (PCP) use which makes it unlikely to have been involved in the sockeye behaviour change. Due to their increases, creosote and CCA represent good candidates. The use of ammoniacal copper arsenate (ACA) was halted in 1999 but was replaced by the similar ammoniacal copper zinc arsenate (ACZA). These two chemicals contain almost the same metals and so in terms of relevance to an effect on sockeye salmon, they could be grouped together to give a steady use throughout the 1990s with a significant increase shown for 1999. Each of these chemicals is discussed below along with a brief note on the toxicity of the metals in CCA, ACA and ACZA.

**Table 13: Comparison of Wood Preservative Active Ingredients Used by Wood Treatment Plants, 1991 to 1999. Data source: Table 11 (ENKON Environmental Limited 2001).**

Active Ingredient	1991 Use (kg)	1995 Use (kg)	1999 Use (kg)	Change from 1991 (kg)
Creosote	2,245,711	5,869,461	5,387,761	+3,142,050
chromated copper arsenate (CCA)	651,134	912,392	923,987	+272,852
Pentachlorophenol (PCP)	789,110	122,966	201,642	-587,468
ammoniacal copper arsenate (ACA)	500	909	not used	-500
ammoniacal copper zinc arsenate (ACZA)	not used	not used	16,488	+16,488

### 7.1 CREOSOTE

Creosote is a complex mixture containing over 90% cyclic aromatic compounds. PAHs make up 85% of the cyclic aromatics, 10% are phenolics and 5% includes oxygen, sulfur, or nitrogen heterocyclics (Padma et al. 1998). Table 17 in the section on PAHs lists the major components of Canadian-produced creosote along with available toxicity data. The 1993 Priority Substances List Assessment Report (Government of Canada et al. 1993b) concluded that there was insufficient data to determine if creosote impregnated waste is a problem in the Canadian environment. The report did note that railway ties and disposal of railway ties constitutes a major source of creosote to the environment. Furthermore, sites of existing and abandoned heavy-duty wood preservation across

Canada show significant levels of soil and water contamination. More recent work has shown that one-third of the creosote applied to railway ties is emitted during the ties' normal service time (Schaefer 2000).

Recent work in B.C. on heavy-duty wood preservation "best practices" methods have resulted in an estimated 90% decrease in the discharge of contaminated effluent (Environment Canada 1998). Thus the main source of creosote to the environment would be non-point source runoff and the use of creosote impregnated wood in direct contact with the aquatic environment (e.g. dock pilings). Hutton and Samis (2000) note that creosote escape from treated wood in water is generally small. The more significant source is creosote exposed to solar radiation which causes the creosote to become more mobile and can then drip into the aquatic environment. Because of the low solubility of many of the PAHs in creosote, it is generally believed that non-bottom feeding biota would not receive significant exposure to creosote contaminants. However, a recent study has shown that the toxicity of the water soluble fraction of creosote is higher than would be expected from the known PAH content (Padma et al. 1998). The study found that nitrogen heterocyclics made up 70% of the soluble fraction of creosote and these compounds are much more toxic and bioavailable to organisms in the water column. Other chemicals such as phenols, cresols, and xylenols are also present in creosote and may be adding to its toxicity.

## **7.2 CHROMATED COPPER ARSENATE**

Chromated copper arsenate (CCA) is obviously of concern because of the three heavy metals involved in the salts which make up the compound. Chromium, copper, and arsenic are all toxic to fish and heavy metals like copper have been linked to sublethal effects such as olfactory damage and both avoidance and attraction reactions in fish (Hansen et al. 1999a; Hansen et al. 1999b; Hansen 1998). CCA is used in construction of outdoor objects susceptible to fungi and insects such as fenceposts, decking, playground equipment, and structural lumber in direct contact with concrete or the ground (Cox 1991). A recent review of the leaching of CCA (Hingston et al. 2000), notes that this compound is also used in both freshwater and marine docks, pilings, and bulk-heads and that current data on leaching is insufficient to quantify leaching rates. Lebow et al. (1999) noted that copper leached much faster in salt water than in fresh, arsenic slightly the reverse, and chromium appeared unaffected by salinity. Another factor in leaching rate is pH where acidic waters leach metals much more readily than neutral waters (Cox 1991 after Solomon and Warner 1990). A more concentrated source of CCA is the runoff from treatment facilities which in one case exceeded Canadian water quality criteria for arsenic, chromium, and copper despite extensive design and procedural controls at the facility (Cox 1991 after Birge and Black 1979). However, adoption of "best practices" in B.C. is reported to have reduced facility effluent by over 90% (Environment Canada 1998). For this reason, leaching from construction materials in use is likely to be the main source of exposure. Researchers suggest that CCA is more toxic than its component parts which is thought to be a result of synergistic toxicity between copper and chromium (Cox 1991 after Solomon and Warner 1990).

### 7.3 AMMONIACAL COPPER ARSENATE AND AMMONIACAL COPPER ZINC ARSENATE

No information was found on the effects of ACA or ACZA other than the toxicity of their component metals.

### 7.4 METAL TOXICITY

#### 7.4.1 Chromium

Chromium is the least toxic of the three metals in CCA with reported LC<sub>50</sub>s for various species of fish ranging from 17.6 to 249 mg/L (World Health Organization 1994c). Sublethal effects of chromium on fish were not noted.

#### 7.4.2 Arsenic

Arsenic is somewhat more toxic with 48 hour LC<sub>50</sub> values for fish species ranging from 0.5 to 47.9 mg/L (Cox 1991; National Research Council 1977). The toxicity for rainbow trout using 144 hour LC<sub>50</sub> was found to be between 17.9 and 19.1 mg/L (Rankin and Dixon 1994). Possible effects of arsenic include lethality, inhibition of growth, reproduction, and behavioural alteration (World Health Organization 2001b). Fish toxicity notably includes necrotic erosion of the olfactory regions of the head (Rankin and Dixon 1994).

#### 7.4.3 Zinc

Acutely lethal concentrations of zinc for freshwater fish are in the range 0.066–2.6 mg/L; the range for marine fish is 0.19–17.66 mg/L (World Health Organization 2001a). The 96 hour LC<sub>50</sub> for juvenile chinook salmon ranges from 0.039 to 0.122 mg/L (Finlayson and Verrue 1982).

#### 7.4.4 Copper

Copper is toxic to fish with LC<sub>50</sub> values of 0.026 to 0.034 mg/L for juvenile chinook salmon (Finlayson and Verrue 1982). Sublethal effects of copper have been widely studied and can occur in salmonids at levels as low as 0.0007 mg/L up to 0.3 mg/L with alevins, fry and juveniles being the most sensitive life stages. Chinook salmon were found to avoid concentrations of copper as low as 0.0007 mg/L but did not avoid concentrations over 0.044 mg/L likely due to olfactory impairment at higher concentrations (Hansen et al. 1999a; Hansen et al. 1999b; Hansen 1998). River spawning, growth, and survival have been impaired in fish from 0.005 to 0.12 mg/L, and salmonids were among the most sensitive species tested. Copper concentrations ranging from 0.05 to 0.3 mg/L have caused salmon to return downstream from spawning areas without having spawned and have inhibited oxygen uptake, caused gill lesions, kidney damage, and diabetes like symptoms in a variety of fish species (Cox 1991 after Hodson et al. 1979).

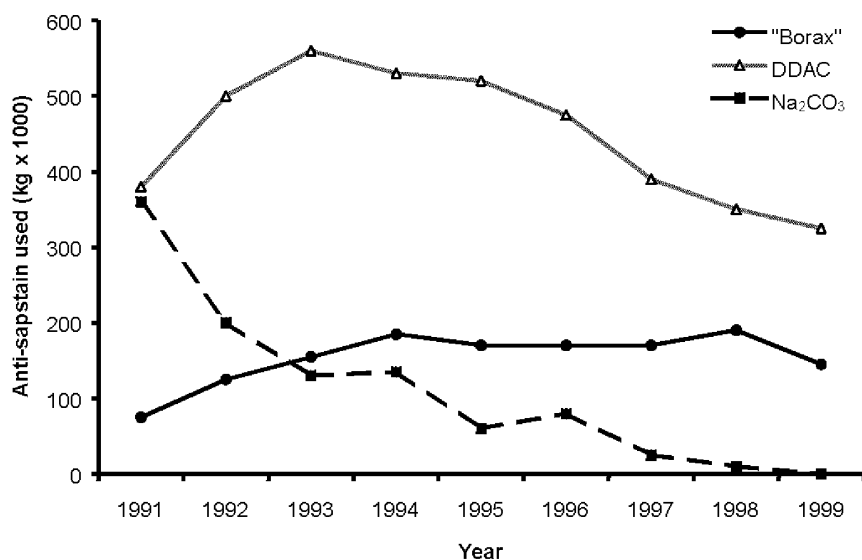
*We could find no data on concentrations of wood preservative chemicals in the Fraser River or in sockeye salmon tissue. The overall use of wood preservatives in B.C. increased significantly during the 1990s. The*

*metals in CCA, ACA and ACZA are known to be highly toxic to fish and may have synergistic effects that make them more toxic in combination. However, Environment Canada estimates that contaminated effluent from heavy-duty wood preservation plants has decreased by 90% in the 1990s. Leaching from wood products therefore represents the main source of these contaminants to the Fraser Basin, although no data are available to quantify this. Wood preservatives remain a potentially significant source of contaminants to sockeye habitat.*



## 8 ANTI-SAPSTAIN COMPOUNDS

Anti-sapstain chemicals are used by lumber mills as short term protection against fungal growth on lumber (and the staining it causes). The six major anti-sapstain chemicals that were used in B.C. during the 1990s are 2-(thiocyanomethylthio)benzothiazole (TCMTB), didecyl dimethyl ammonium chloride (DDAC), 3-iodo-2-propynyl butyl carbamate (IPBC), sodium carbonate, two forms of borate (disodium octaborate tetrahydrate and disodium tetraborate decahydrate) and Azaconazole (ENKON Environmental Limited 2001). Major concerns have been raised about the toxicity of TCMTB (Kruzynski and Birtwell 1994; Nikl and Farrell 1993; MacKinnon and Farrell 1990), IPBC (Farrell et al. 1998; Farrell and Kennedy 1999; Szenasy 1999), and DDAC (Farrell and Kennedy 1999; Johnston et al. 1998; Szenasy 1999) to salmonids. These studies are in addition to the B.C. MELP reports on each of these three compounds: TCMTB (Hanssen et al. 1991), DDAC (Henderson 1992a), and IPBC (Henderson 1992b). Perhaps as a result of this data and increasing regulation and “best practices” procedures, the use of all anti-sapstain compounds in B.C. has been either decreasing or remaining fairly constant since the mid to early 1990s (Figures 12 and 13). For this reason, none of these compounds alone is considered high priority for a possible cause of the late-run sockeye behaviour change.



**Figure 12.** Change in use of anti-sapstain active ingredients “Borax” (two borate compounds), DDAC and sodium carbonate used in B.C. from 1991-1999. Data source: (ENKON Environmental Limited 2001).

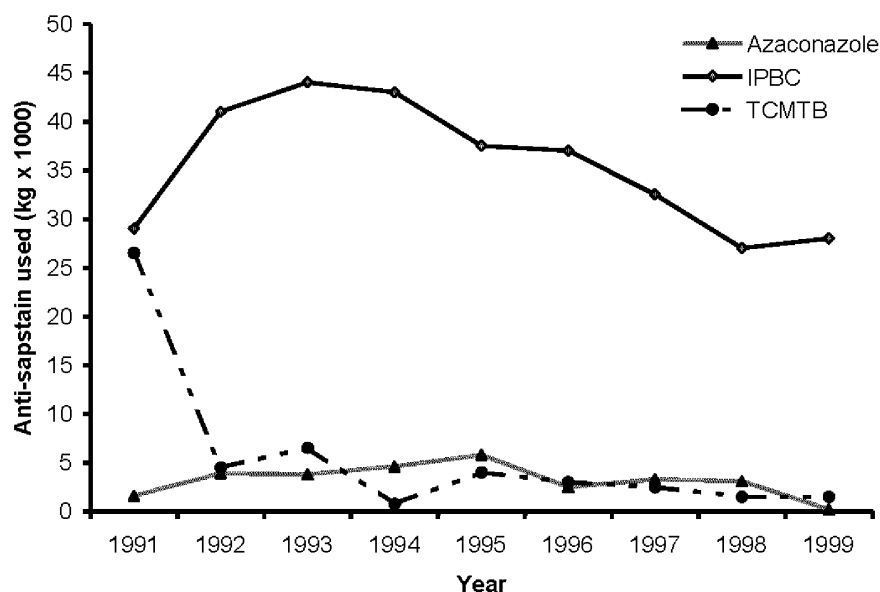


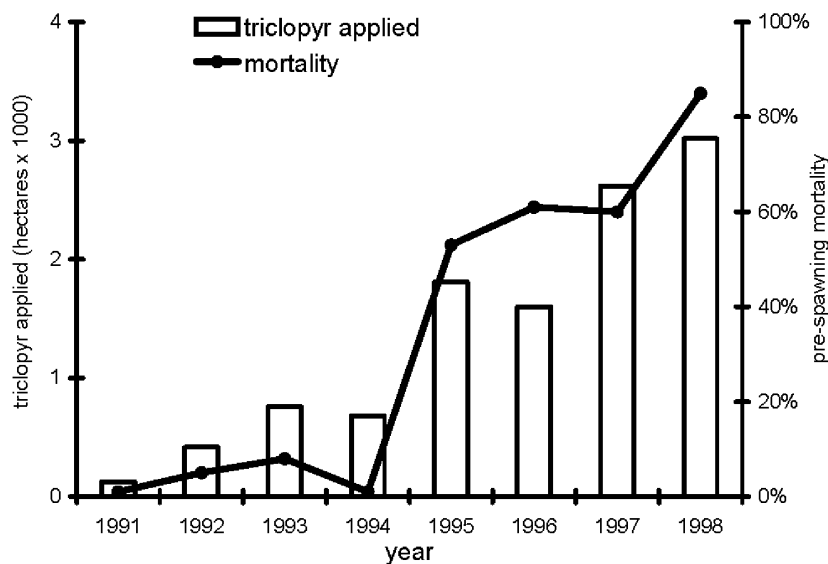
Figure 13. Change in use of anti-sapstain active ingredients Azaconazole, IPBC, and TCMTB used in B.C. from 1991-1999. Data source: (ENKON Environmental Limited 2001).

*No data could be found on concentrations of antisapstain chemicals in the Fraser River or in sockeye salmon tissues. Data show that these chemicals have lethal and sublethal effects on fish. Data on the use of these chemicals shows an overall decrease or relatively constant use in the 1990s. This, combined with increasing provincial “best practices” enforcement suggests that these compounds not be considered high priority for possible involvement in the sockeye behaviour change. The consistent use of the borate compounds, DDAC and IPBC merits some concern.*

## 9 FORESTRY CHEMICALS

### 9.1 PESTICIDES

The forestry industry use of pesticides is not covered in the Survey of Pesticide Use in British Columbia: 1999 (ENKON Environmental Limited 2001). This may be because industry may purchase directly from manufacturers outside of B.C., such that sales figures would not be included in the B.C. survey. Data on pesticides used by the forestry industry was obtained from the National Forestry Database Program (Canadian Council of Forest Ministers 2001). These data provide the number of hectares treated by a given chemical in one year for each province from 1988 to 1999. The use of the insecticide *Bacillus thuringiensis* in B.C. varies widely from year to year and does not correlate at all with behaviour changes in Fraser River sockeye. Other insecticides are grouped into one category and show a steady decline from 1992 to insignificant use by 1998. The application of the herbicides 2,4-D, hexazinone, and those in the 'other' category also show a steady decline to little or no use by the forestry sector by the late 1990s. The use of the herbicide glyphosate is highly variable with the highest application years in 1989 to 1993. However, data for the use of triclopyr on B.C. forests shows an increase from 1991 to 1998, contemporaneous with increases in Fraser River late-run sockeye pre-spawning mortality as shown in Figure 14.



**Figure 14.** Graph of late-run sockeye pre-spawning mortality (line) and forestry application of triclopyr versus year from 1991 to 1998. Although no causal link can be established between triclopyr use and the sockeye crisis, a contemporaneous association between these is a concern. Data sources: (Lapointe 2002 and Canadian Council of Forest Ministers 2001).

This is not the first example in Canada of an apparent correlation between forestry pesticide application and a resulting effect on fish. Fairchild et al. (1999) found that a significant proportion of the lowest salmon catches in part of Atlantic Canada coincided with the spraying of the insecticide Matacil 1.8D. Their final hypothesis was that the surfactant 4-nonylphenol was the causal agent and that it probably acted through endocrine disruption. Experimental evidence to support the correlation is pending.

There are a few reasons to doubt the involvement of triclopyr in the sockeye behaviour change. The apparent correlation in Figure 14 may be coincidental, particularly as this data is for all of B.C., not just for the Fraser River watershed. The validity of this relationship could be further tested by obtaining the statistics of triclopyr use within the Fraser River watershed and, if possible, the dates of application. Furthermore, the method of application of triclopyr in B.C. is known as basal bark treatment and is a ground based treatment method that is carefully controlled and regulated (Boateng 2002; personal communication). It is difficult to tie the B.C. wide use of a ground applied chemical to a behavioural change in an aquatic organism. Data on the effects of sockeye exposure to triclopyr is clearly needed.

Triclopyr is a pyridine compound used as a selective systemic herbicide to control unwanted woody and broadleaf plants. The commercial formulation in Canada is called Release™ and is manufactured by Dow AgroSciences Canada Inc. The parent compound and the amine salt are practically non-toxic to fish with a 96 hour LC<sub>50</sub> value of 117 mg/L for rainbow trout (United States Environmental Protection Agency 1998). Of greater concern are the ester form of triclopyr (found in Garlon 4™ and Release™) and triclopyr's most common degradation product 3,5,6-trichloro-2-pyridinol (TCP). Table 13 shows the 96 hour toxicity data from Wan et al. (1987) for juvenile sockeye salmon.

**Table 14: The 96 hour LC<sub>50</sub> values for sockeye salmon of various forms and formulations of triclopyr and its major degradate TCP. Data source: (Wan et al. 1987).**

Test Chemical	Sockeye 96 hour LC <sub>50</sub> (mg/L)
Garlon 3A™	311
Garlon 4™	1.4
Triclopyr ester	0.4
Triclopyr acid	7.5
Pyridinol (TCP)	2.5

It should be noted that Garlon 4™ (US formulation) contains 48% butoxyethyl ester of triclopyr while Garlon 3A™ contains the amine salt form (Wan et al. 1987). The Canadian formulation Release™ contains 61.6% butoxyethyl ester (Dow AgroSciences Canada Inc. 2000). Thus its LC<sub>50</sub> value should be slightly lower (more toxic) than that of Garlon 4™. Triclopyr is not strongly adsorbed to soil particles and so is considered mobile. Its half life in soil ranges from 30 to 90 days while the half life of TCP ranges from 8 to 279 days (longer in cold or arid conditions). Sublethal effects of Garlon 4™ on rainbow trout have been noted as low as 0.6 mg/L with avoidance reactions at 19.2 mg/L (Morgan et al. 1991). Information on sublethal effects on fish were not found for TCP

but it has been linked to risk of a disruption of the development and maturation of the nervous system in fetuses, infants and children (Cox 2000 after Das and Barone 1999).

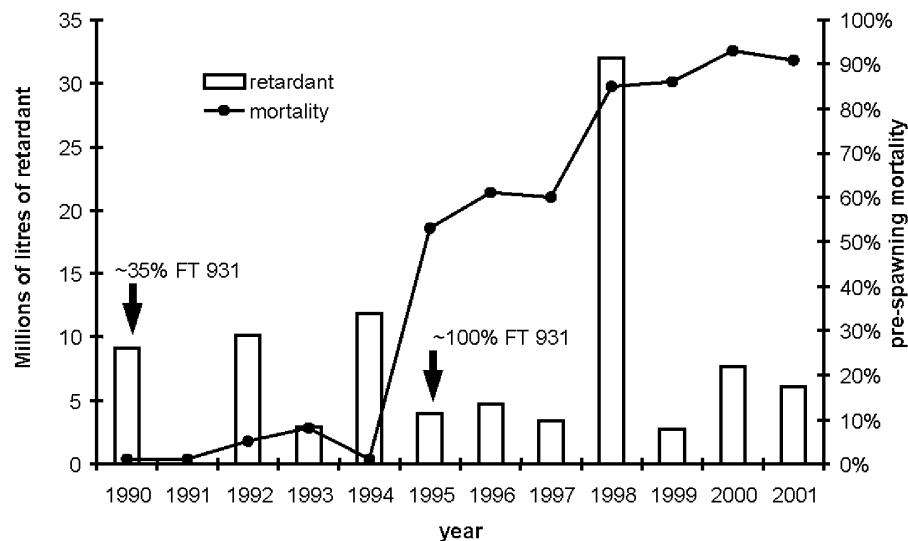
## 9.2 FIRE CONTROL CHEMICALS

Every year forest fires in B.C. threaten lives, property and forest lands. These fires are fought with a variety of complex mixtures including short term fire suppressants (foams) and long term retardants (chemical salts). Most of the long term retardant mixtures involve diammonium phosphate, ammonium sulphate, ammonium phosphate, and/or ammonium polyphosphate as the active fire retardant. These salts chemically react with the products of combustion causing incomplete combustible products to be formed. "The salt permits decomposition of the fuel at a lower temperature thereby promoting the formation of water, carbon monoxide and char, at the expense of the flammable gases" (Fire-Trol Canada 2001). The toxicity of the fire retardant salts is considered very low to insignificant (100-10,000 mg/L) (Gaikowski et al. 1996), and is caused by un-ionized ammonia released into the water. The fire suppressant foams are more toxic (10-100 mg/L) because of the surfactants used to make the bubbles of the foam small and durable (Gaikowski et al. 1996).

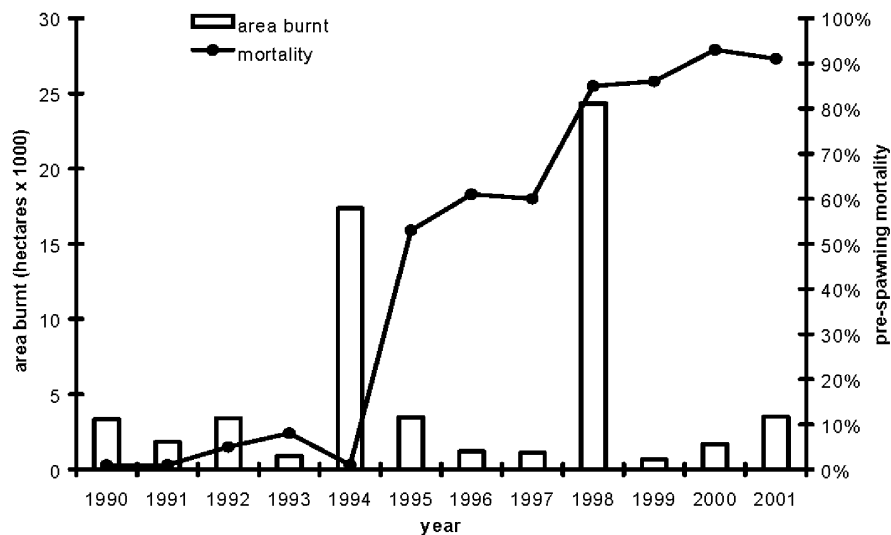
The long term retardants can be made more toxic by the addition of other ingredients. Most of the fire retardant salts are highly corrosive and so the mixtures have a corrosion inhibitor added to protect the storage containers and fire fighting equipment. In the case of retardants like Fire-Trol® 931 the corrosion inhibitor used is yellow prussiate of soda (YP Soda or sodium ferrocyanide). Studies have shown that when sodium ferrocyanide is exposed to sunlight it produces cyanide, which can make dilute solutions of sodium ferrocyanide highly toxic to fish (Norris et al. 1983; Little and Calfee 2000; Burdick and Lipschuetz 1950). Although this process has been known for some time, a recent report by the U.S. Geological Survey prepared for the U.S. Department of Agriculture Forest Service has shown that toxicity of formulations with YP Soda can cause up to a 100-fold increase in toxicity to rainbow trout (Little and Calfee 2000). The result of this report was a national Stop Work Order issued to Fire-Trol Holdings, L.L.C. on March 28, 2000. After two weeks of consultation between a variety of U.S. government agencies, a Resume Work Order was issued with the commitment by all agencies to conduct further research, particularly in the field (USDA Forest Service 2000).

This information is significant since high use years for fire retardants in B.C. correspond with jumps in the pre-spawning mortality of late-run sockeye. Figure 15 shows the 1995 jump in mortality was preceded by a fairly high retardant use year in 1994. In 1998 the jump in mortality coincides with a very high retardant use year. There are, however, many years prior to 1994 in which high volumes of fire retardant were used. However, the use of Fire-Trol® 931 (FT 931 in Figure 15) increased over time from an estimated 35% of retardant used in 1990, to become the almost exclusive retardant used by 1995 (Bell 2002, personal communication). Thus, in the years before 1994, the amount of YP Soda in the fire retardants used might have been quite small. Again this data covers fire retardant use in all of B.C. and large fires are quite common in the northern parts of B.C. which would not affect the Fraser River watershed. In order to address this problem with available data, the number of hectares of forest burnt per year according to forest district was obtained from B.C. Ministry of Forests Annual Reports (British Columbia Ministry

of Forests 2002). Figure 16 shows that the years 1994 and 1998 were major forest fire years in the Cariboo and Kamloops forest districts. This suggests that efforts to combat these fires would be in the right area to affect the Fraser River and its tributaries. The unknown factors of persistence and mobility of the fire retardants could explain the continuation of the mortality during years of mild fire activity. The specific timing of the fires and distance from water could explain the lag of mortality in 1994/1995 which is not seen in 1998. However, the correlation is poor and there is no clear evidence that the retardant is used heavily in the Fraser River watershed. Data on the presence of sodium ferrocyanide or its breakdown products in the Fraser River or in sockeye fish tissues is needed to assess the possibility of this contaminants role in the sockeye behaviour change.



**Figure 15.** Graph of late-run sockeye pre-spawning mortality (line) and forestry application of fire retardant versus year from 1990 to 2001. Although no causal link can be established, note the contemporaneous increase of both parameters in 1998 versus the apparent time lag between application of retardant and mortality in 1994. Data sources: (Lapointe 2002 and Bell 2002).



**Figure 16.** Graph of late-run sockeye pre-spawning mortality (line) and area of forest burnt in the Cariboo and Kamloops forest districts versus year from 1990 to 2001. Note the decrease in fires in years other than 1994 and 1998. Data sources: (Lapointe 2002 and British Columbia Ministry of Forests 2002).

*No data were found on the presence of triclopyr or cyanide compounds in the Fraser River or in sockeye salmon tissues. Data on use of these chemicals by the forestry industry in B.C. suggests possible correlations with sockeye mortality, but the data are not specific to the Fraser River watershed. The current information on forest practices also suggest that these chemicals should not be reaching the Fraser River. However, the widespread use of these chemicals remain a potential risk to sockeye salmon, particularly in light of the recent disruption of late-run sockeye migration.*





## 10 ANTHROPOGENIC COMPOUNDS IN SEWAGE

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While agricultural and industrial contaminants have been, and continue to be, a widely studied environmental problem, the presence of chemicals from domestic and veterinary uses has gone relatively unnoticed (Daughton and Ternes 1999). With the growing understanding of sublethal effects, such as endocrine disruption, that can occur at very low concentrations, contaminants that were previously ignored are attracting increasing interest.

### 10.1 NATURAL HUMAN HORMONES

There is currently great interest in natural and artificial estrogens and their endocrine disrupting potential. A recent study in the United Kingdom found that estrogenic substances found in sewage effluents are predominantly natural estrogens, and that the estrogen excreted by humans is largely inactive but is activated via sewage treatment processes (Henderson 1997). Little information is available on the concentrations and effects of natural hormones in treated and untreated sewage.

### 10.2 PHARMACEUTICAL AND PERSONAL CARE PRODUCTS

Many of the unintended effects of drugs, perfumes, surfactants and other products are unknown though acute toxicity and endocrine disruption have been demonstrated for some (Daughton and Ternes 1999). Some attention has recently been paid to musks used to scent products. Nitro musks were first introduced in the late 1800s and have been widely used as synthetic fragrances. They were joined by polycyclic musks in the 1950s (Daughton and Ternes 1999; Rimkus 1999). Both groups have been found in water, sediments and biota throughout the world (Daughton and Ternes 1999; Rimkus 1999; Rimkus et al. 1999; Chou and Dietrich 1999). Nitro musks are being phased out in some parts of the world due to toxicity concerns (Daughton and Ternes 1999). In particular, recent work has shown that the amino metabolites of nitro musks produced by sewage treatment are more toxic and endocrine disruptive than the parent compounds (Rimkus et al. 1999; Chou and Dietrich 1999). The production of polycyclic musks has increased up to a 1999 worldwide production of roughly 6000 t/year (Rimkus 1999). Environmental samples now contain higher concentrations of the polycyclic musks than of the major nitro musks and they are believed to be persistent and lipophilic. However, toxicity data on the polycyclic musks is lacking (Rimkus 1999).

Table 15 lists some of the known pharmaceutical and personal care compounds of concern. Current data does not allow the assessment of these chemicals as potential causes of the sockeye behaviour change. A survey of pharmaceutical use in the style of the B.C. pesticide survey could be done using such resources as the B.C. Pharmanet database (Addison 2002, personal communication). The U. S. Geological Survey recently released information on these chemicals analyzed in their nation wide survey (Kolpin et al. 2002), which suggested that detergent metabolites, plasticizers, steroids and non-prescription drugs were found at relatively high concentrations in streams. The most commonly detected substances were antibiotics, reproductive hormones, and a mix of prescription drugs. These findings strongly suggest that these products will also be found

in the Fraser River, considering both the number and size of communities that release municipal effluent into it.

*Although no data exist which would allow for an assessment of sewage compounds including hormones, pharmaceuticals, and personal care products, it is becoming increasingly clear that these chemicals are prevalent in high population areas. These products represent an unknown risk but clearly merit scrutiny.*

**Table 15: Pharmaceutical & Personal Care Products of concern. Data source: (Daughton and Ternes 1999).**

Compound	Use/origin	Compound	Use/origin
Acetaminophen	Analgesic/anti-inflammatory	Acetylsalicylic acid	Analgesic/anti-inflammatory
Betaxolol	Beta-blocker	Bezafibrate	Lipid regulator
Biphenylol	Antiseptic, fungicide	Bisoprolol	Beta-blocker
Carazolol	Beta-blocker	Carbamazepine	Analgesic/antiepileptic
4-chloro-3,5-xyleneol	Antiseptic	Chlorophene	Antiseptic
Clenbuterol	Bronchodilator	Clofibrate	Lipid regulator
Clofibric acid	Metabolite of lipid regulators	Cyclophosphamide (Cyclophosphane)	Antineoplastic
Diatrizoate (Na)	X-Ray contrast media	Diazepam	Psychiatric drug
Diclofenac-Na	Analgesic/anti-inflammatory	Dimethylaminophenazone (Aminopyrine)	Analgesic/anti-inflammatory
17 $\alpha$ -Ethinyl estradiol	Oral contraceptive	Etofibrate	Lipid regulator
Fenfluramine	Sympathomimetic amine	Fenofibrate	Lipid regulator
Fenofibric acid	Metabolite of fenofibrate	Fenoprofen	Analgesic/anti-inflammatory
Fenoterol	Bronchodilator		Antibiotics
Fluoxetine	Antidepressant	Fluoroquinolone carboxylic acids	
Gemfibrozil	Lipid regulator	Fluvoxamine	Antidepressant
		Gentistic acid	Metabolite of acetylsalicylic acid
o-Hydroxyhippuric acid	Metabolite of acetylsalicylic acid	Ibuprofen	Analgesic/anti-inflammatory
Ifosfamide	Antineoplastic	Indomethacine	Analgesic/anti-inflammatory
Iohexol	X-Ray contrast media	Iopamidol	X-Ray contrast media
Iopromide	X-Ray contrast media	Iotrolan	X-Ray contrast media
Ketoprofen	Analgesic/anti-inflammatory	Meclofenamic acid	Analgesic/anti-inflammatory
Methylbenzylidene camphor	Sunscreen agent	Metoprolol	Beta-blocker
Musk ambrette	Synthetic nitro musk	Musk xylene	Synthetic nitro musk
Musk ketone	Synthetic nitro musk	Musk moskene	Synthetic nitro musk
Tibetene	Synthetic nitro musk	Galaxolide	Polycyclic musk
Tonalide	Polycyclic musk	Celestolide	Polycyclic musk
Musk xylene derivatives	Amino musks	Nadolol	Beta-blocker
Naproxen	Analgesic/anti-inflammatory	Paroxetine	Antidepressant
Phenazone (Antipyrine)	Analgesic	Propanolol	Beta-blocker
Propyphenazone	Analgesic/anti-inflammatory	Salbutamol (albuterol)	Bronchodilator
Salicylic acid	Metabolite of acetylsalicylic acid	Sulfonamides	Antibiotics
Terbutaline	Bronchodilator	3,4,5,6-Tetrabromo-o-cresol	Antiseptic, fungicide
Timolol	Beta-blocker	Tolfenamic acid	Analgesic/anti-inflammatory
Triclosan	Antiseptic	Verpamil	Cardiac drug



## 11 POLYCYCLIC AROMATIC HYDROCARBONS

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### 11.1 BACKGROUND

Polycyclic aromatic hydrocarbons (PAHs) are organic compounds consisting of at least two joined aromatic (benzene) rings. These rings consist of five or six carbon atoms with hydrogen atoms, alkyl groups, or other radicals attached to the ring structures. PAHs are generally categorized according to the number of aromatic rings: low molecular weight (three or less rings) and high molecular weight (four or more rings). PAH compounds generally have high molecular weight, low solubility, are hydrophobic, and adsorb to particulate matter. Hoffman et al. (1984) estimated that 79-93% of high molecular weight PAHs are found in association with particulate matter. There are over 2000 PAH compounds known (Pawluk et al. 1998), but only 16 have been placed on the USEPA list of priority pollutants and only 13 have been assessed by Environment Canada (Government of Canada et al. 1994c). The USEPA has ranked PAHs third for risk potential among chemical groups found in contaminated sediments (after pesticides and PCBs) (United States Environmental Protection Agency 1996a). Both Canadian and US agencies are making these assessments based on limited knowledge as the sublethal effects of PAHs are still being assessed and there is some dispute over whether a sublethal effect is necessarily a harmful effect (Payne et al. 1988).

### 11.2 SOURCES

PAHs are largely produced as by-products from the combustion of organic matter which are then released to the atmosphere. For this reason, atmospheric deposition is thought to be by far the major source of PAHs to the environment. Table 16 summarizes the estimated volume of PAHs released to the atmosphere in Canada in 1990 (Government of Canada et al. 1994c after LGL Ltd. 1993). It should be noted that forest fires contribute 47% of the atmospheric load with aluminum plants contributing another 21% and home wood heating a further 11%. Thus 79% of the atmospheric load of PAHs come from three sources. Recent work using Principal Component Analysis (PCA) on suspended particulates and sediments of the Fraser River system attributes sources of PAHs in urban areas to dominantly petroleum combustion, while more remote areas are dominated by biomass (e.g. wood and grass) burning (Yunker et al. in press).

The aquatic environment also receives PAHs directly from the use and spillage of petroleum products, coal and creosote. As noted in the pesticide section, the use of creosote as a wood preservative increased dramatically from 1991 to 1999 (ENKON Environmental Limited 2001). Effluent from industry, municipal wastewater, landfill leachate, storm sewers, and surface runoff also provide PAHs to the aquatic environment.

Work by Sekela et al. (1995) found that PAHs were not present in organically rich solids from the Fraser and Thompson pulp mill effluents, but were found in solids from the sewage treatment plant in Prince George. In general, samples from the Fraser and Thompson Rivers above Hope (Sekela et al. 1995) did not contain PAHs exceeding guidelines established by B.C. MELP. A study conducted for Environment Canada (ENKON Environmental Limited 1999) determined that the average annual loading of PAHs to the Georgia Basin from wastewater effluents alone is 821 kg. The study noted

that 81% of this came from stormwater discharges, 18% from municipal wastewater treatment plants, and 1% from petroleum refinery discharges. Yunker et al. (1999) determined that the Fraser River is the predominant source of both natural and anthropogenic PAHs to the Georgia Basin. Furthermore, all parts of the Fraser Basin exhibit levels of PAHs in excess of “pristine” background levels. PAH concentrations were found to exceed provincial or interim federal sediment quality guidelines in the City of Kamloops, in most of the post-1970 core sections from Kamloops Lake, in most locations in the Fraser estuary and Vancouver Harbour, and in all of the sections analysed in two cores from the Strait of Georgia. Some of these PAHs are attributed to atmospheric input but most input was attributed to runoff, municipal treatment plants, and industrial effluent. A summary of recent work by Garrett and Shrimpton (2000) noted that samples in the 1980s and early 1990s around Vancouver and Victoria harbours and the Fraser River have shown PAH levels comparable to heavily contaminated sites elsewhere in the world. These findings strongly suggest that PAH levels in urban parts of B.C. are rising.

**Table 16: Annual atmospheric emissions of PAHs in Canada during 1990. Data source: (Government of Canada et al. 1994c after LGL Ltd. 1993).**

Sources	PAH releases	
	tonnes	% of total
<b>Anthropogenic Sources</b>		
Industrial Processes		
Aluminum plants	925	21
Metallurgical (including ferro-alloy)	19.5	0.4
Coke production	12.8	0.3
Petroleum refineries	2.5	0.1
<b>Combustion Sources</b>		
Residential Heating		
Wood	474	11
Others	29	0.7
Open air fires/agricultural burning	358	8.3
Incineration		
Teepee burners	249	5.8
Municipal (with sludges)	1.3	<0.1
Industrial	1.1	<0.1
Transportation		
Diesel	155	3.6
Gasoline	45	1
Other	1.2	<0.1
Thermal Power Plants	11.3	0.3
Industrial Combustion		
Wood	5.7	<0.1
Other	10.2	0.2
Commercial and Institutional Heating	2.7	0.1
Cigarettes	0.2	<0.1
<b>Natural Sources</b>		
Forest Fires	2010	47
<b>Total</b>	<b>4314</b>	<b>100</b>

### 11.3 TOXICITY

Sublethal effects of PAHs on salmonids include neurosensory damage, increased oxygen consumption, and the impairment of neurotransmission, muscle contraction and osmoregulation (Neff 1979). These effects can be seen at concentrations ten-fold or more below acute toxicity thresholds. Studies of pink salmon following the Exxon Valdez oil spill showed surprising persistence of the oil (up to 4 years) and high vulnerability of salmon embryos to PAHs (Rice et al. 2001). It was determined that long term exposures of embryos to very low levels of PAHs (a few ppb) would have negative effects. Table 17 lists the toxicity concentration data summarized by the Priority Substance List Assessment Report (Government of Canada et al. 1994c) along with the most recent Canadian Water Quality Guidelines for the Protection of Aquatic Life (Canadian Council of Ministers of the Environment 2001).

**Table 17: PAH presence in creosote, Canadian Water Quality Guidelines, and reported toxicity. Data sources: (Government of Canada et al. 1994c; Canadian Council of Ministers of the Environment 2001 and Wilson 2002, personal communication).**

Polycyclic aromatic hydrocarbon (PAH)	% in Creosote	Freshwater Quality Guideline ( $\mu\text{g/L}$ ) <sup>1</sup>	Reported Toxicity ( $\mu\text{g/L}$ ) <sup>2</sup>
Naphthalene	17.5	1.1	27-d LC <sub>50</sub> = 110
Phenanthrene	10.2	0.4	90-d LOEC = 8
Fluoranthene	9.9	0.04	14-d LOEC = 38
Acenaphthene	5.6	5.8	2-d LC <sub>50</sub> = 60
Fluorene	5.1	3.0	14-d LOEC = 125
Pyrene	4.4	0.025	48-h LC <sub>50</sub> = 91
Anthracene	2.3	0.012	96-h LC <sub>50</sub> = 6.6
Carbazole	2.1		
Acenaphthylene	2.0		2-d LC <sub>50</sub> = 60
Benz(a)anthracene	1.1	0.018	14-d LOEC = 5
Chrysene	1.0	Insufficient data	
Benzo(b)fluoranthene	0.6		
Benzo(k)fluoranthene	0.4		
Dibenz(a,h)anthracene	0.2		
Benzo(g,h,i)perylene	0.1		
Ideno(1,2,3-c,d)pyrene	0.1		
Benzo(a)pyrene		0.015	96-h LC <sub>50</sub> = 5
Acridine		4.4	
Quinoline		3.4	

*1 From the Canadian Water Quality Guidelines for the Protection of Aquatic Life. No marine data currently available.*

*2 LOEC refers to Lowest Observed Effect Concentration*

*Samples from the upper reaches of the Fraser River do not exceed current guidelines for PAHs. However, sediment data from the lower Fraser show high levels of contamination. Many sources of PAHs are linked to human population size which increased steadily during the 1990s. It is unclear whether PAHs in Fraser River water are of toxicological concern to late-run sockeye salmon, but the lack of data for PAHs in sockeye tissue render it difficult to speculate. The increasing industrialization of the Fraser Basin suggest that PAHs are likely to represent a class of compounds that will present an increasing risk to Fraser Basin salmon stocks.*



## 12 PERSISTENT ORGANIC POLLUTANTS (POPS)

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Persistent organic pollutants (POPs) are also known for their toxicity and potential for bioaccumulation such that they are also often called PBT compounds (persistent, bioaccumulative and toxic). Many POPs are halogenated and have low water solubility (hydrophobic) and high lipid solubility (lipophilic) which explains their tendency to bioaccumulate in fatty tissues (Paasivirta 1998). These compounds are often divided into “legacy” (or “classic”) POPs and “new” POPs largely based on when their toxicity and persistence were discovered or when their use became significant, rather than when they were first manufactured.

### 12.1 “LEGACY” POPS

The “legacy” POPs include compounds that were produced in large amounts in the 1950s and 1960s, but growing awareness of their hazardous properties led to restrictions and bans through the 1970s and 1980s in North America and Europe. Some of the most common and problematic members of this class of chemicals include polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins (dioxins), polychlorinated dibenzofurans (furans), hexachlorobenzene (HCB), pentachlorophenol (PCP) and the OC pesticides (e.g. DDT, aldrin, dieldrin, endrin, chlordane, heptachlor, mirex, lindane, and toxaphene).

Today the concentrations of many of these compounds are declining or stable (Macdonald et al. 1992 and 1998) though there are many highly contaminated locations which will take many years to remediate. The persistence and bioaccumulative properties of these compounds mean that they tend to remain in food chains for very long periods. It has also been shown that these compounds can travel long distances in the atmosphere before being re-deposited (Wilkening et al. 2000). Dioxins and furans have been detected in stream bed sediments upstream of pulp mills in Prince George at levels above accepted guidelines. The location and congener profile of these samples support an airborne source (Sekela et al. 1995).

There is a documented “distillation effect” of the more volatile POPs whereby the contaminants tend to volatilize in warm locations (low latitudes) and condense out of the atmosphere at higher latitudes and altitudes (Simonich and Hites 1995). It is now recognized that the “distillation effect” is actually the result of a variety of processes that transport and concentrate contaminants based on the interaction of their physical and chemical properties with environmental conditions (Macdonald et al. 2002). The results of these processes are demonstrated by the high concentrations of certain POPs found far from any possible source in the Arctic and in B.C. mountain lakes and snow (Blais et al. 1998; Campbell et al. 2000). This long range transport makes the use of these compounds a global issue since their continued use in parts of Russia and Asia results in their deposition in the North American and Arctic environment (Wilkening et al. 2000).

Although levels of “legacy” POPs are declining in a number of indicator organisms in North America (British Columbia Ministry of Environment 2000), this may not be true of Fraser River salmon. The long-range transport of atmospheric POPs is causing detectable levels in the open ocean environment. A recent U.S. study suggests that the majority of

salmonid body burden of “legacy” POPs comes from the time spent in the ocean environment (O'Neill et al. 1998). This conclusion is supported by unpublished data from Fisheries and Oceans Canada (Ross 2002, personal communication) which compare outmigrating chinook smolts with returning adults and show that an appreciable load (>90%) of POPs are gained by the fish in the open ocean rearing environment. The outmigrating smolts also show a high concentration of POPs. This may be attributed to a number of sources, including atmospheric. It has recently been recognised that commercial fish feeds used in hatcheries contain appreciable levels of PCBs and other POPs (Ikonomou et al. 2002a, Ikonomou 2001). Also, since POPs are lipophilic they can be passed from the adult female to the concentrated food stores in the eggs (Giesy et al. 1999). Thus the next generation of salmon begin life with an existing POP burden. A study in Alaska showed that salmon transported POPs from the open ocean into spawning lakes where local fish showed elevated concentrations relative to fish in a nearby lake with no anadromous fish (Ewald et al. 1998). Another migration related POP issue is that anadromous fish use up a large portion of stored fat during their return migration because they stop feeding and focus on migrating (Foshaug et al. 2000). A remobilization of stored lipophilic POPs in returning late-run sockeye salmon represents a plausible scenario for a possible contaminant-related impact on behaviour and migratory timing. A study of the Fraser River (Sekela et al. 1995), found that levels of dioxins and furans exceeded bed sediment guidelines (Canadian Council of Ministers of the Environment and B.C. Ministry of Environment, Lands and Parks) both upstream and downstream of pulp mill sources. This and the congener profile indicate significant airborne transport of POPs into the Fraser River watershed. For all these reasons, Fraser River salmon may be experiencing higher levels of POPs than other biota in the same ecosystem.

## 12.2 “NEW” POPS

The “new” POPs are toxic and persistent compounds that have been introduced more recently and in most cases have not yet been regulated or banned.

### 12.2.1 *Brominated Flame Retardants*

Brominated flame retardants consist of roughly 70 chemicals which have a global consumption of over 300,000 t (Arias 2001). Approximately  $\frac{3}{4}$  of this worldwide market is concentrated in two brominated chemical types: tetrabromobisphenol A (TBBPA) and its derivatives (>150,000 tpa) and polybrominated diphenyl ethers (PBDEs) and its congeners (~100,000 tpa) (Arias 2001). Polybrominated biphenyls (PBBs) were a major brominated flame retardant until a disaster in Michigan involving the accidental addition of this compound to animal feed resulted in the destruction of millions of farm animals. In 1974, as a result of this incident, the U.S. production of the PBB involved was halted and by 1979 production of all PBBs ceased. Germany followed suit in 1985 and currently only France is known to produce any PBBs (World Health Organization 1994a). TBBPA is not found extensively in the literature, likely because, despite its high production rate, it is not commonly found in biota, including fish (Hakk 2001). On the other hand, PBDEs stand out among the “new” POPs as being of high concern and are found throughout the current literature dominating the abstracts from the 2001 Second International Workshop on Brominated Flame Retardants.

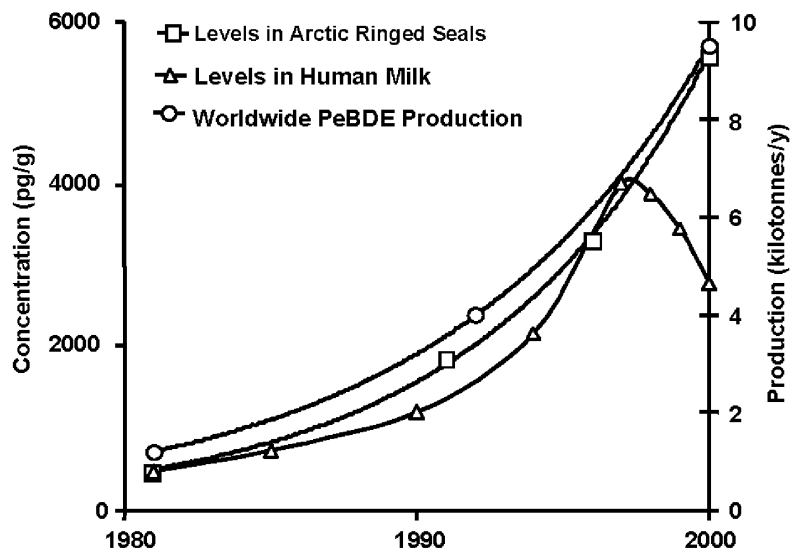


Figure 17. Comparison of PBDE levels in ringed seals from the Canadian arctic, PBDE levels in human breast milk from Sweden, and worldwide commercial penta-BDE production. Figure source: (Ikonomou et al. 2002b).

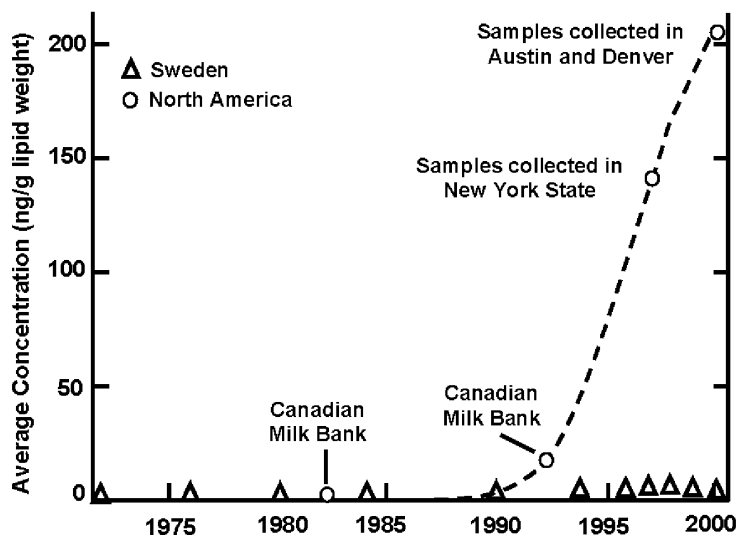


Figure 18. Graph of recent PBDEs in human breast milk data from North America with comparison to the same data from Sweden as in Figure 17. Figure source: (modified from Betts 2002).

The interest in PBDEs has been highlighted by a study in Sweden showing an exponential increase of PBDEs in human breast milk from 1972 to 1997 (Norén and Meironyté 2000; Meironyté et al. 1999). A follow up to this study has shown a sudden decrease in levels in 1998, 1999 and 2000 as shown in the triangles on Figure 17 (Meironyté Guvenius et al. 2001). This decrease is attributed to the phase out of PBDEs in Sweden which is to be backed up by an official ban proposed by the National Swedish Chemicals Inspectorate in 1999 (Edie newsroom 2000). However, the use of PBDEs has not been banned or restricted in North America. As of the mid 1990s, North America had accounted for 40% of the world wide demand for these products for use in electronic circuit boards, furniture, building materials, textiles, carpets, and vehicles (Manchester-Neesvig et al. 2001). In 1999, the North American portion of demand had risen to 51% even as the volume of world demand had risen from 40,000 t in 1992 to 67,125 t in 1999 (Hale et al. 2001). Not surprisingly, levels of these compounds are found to be increasing in the North American environment. In particular, biota in the Canadian Arctic are showing this exponential increase along with world production as shown in Figure 17 (Ikonomou et al. 2002b; Ikonomou et al. 2000; Stern and Ikonomou 2000). Biota from the B.C. coast and water from the Fraser River also show the presence of these chemicals (Ikonomou et al. 2002c). Myrto Petreas reported at the American Chemical Society Meeting in March 2001 the highest PBDE level found in the adipose tissue of any woman to date at an average of 85.7 ng/g of fat (Betts 2001). Figure 18 shows the levels of PBDEs recently reported for North American human breast milk. Note that the scale is 1000x the scale of Figure 17. This means that levels in North American breast milk are 40x higher than the highest levels reached in Sweden (Betts 2002). The North American data in Figure 18 must be interpreted with caution as the data sources are geographically far apart. Thus the line connecting the points is perhaps misleading as there are no time series data within one area to show a trend. However, that there are very high levels of PBDEs in North Americans is undisputable.

Brominated diphenyl ethers represent a group of compounds based on two aromatic rings on which one to 10 of the hydrogen atoms can be replaced by bromine atoms. This results in 209 different possible congeners, which are grouped according to the number of hydrogen atoms replaced (mono- to deca-BDE). There are three commercial formulations currently available, consisting of mixtures of congeners containing three to 10 bromine substituted positions. These formulations are named after the dominant congener (Table 18) with the exception of octa-BDE which is dominantly made up of the hepta congener.

World production of the three current formulations in 1999 is estimated at 80% deca-BDE, 14% penta-BDE, and 6% octa-BDE out of a total of 67,125 t (Arias 2001; Hale et al. 2001). Although deca-BDE is the most used compound, environmental samples tend to show a pattern of congeners similar to penta-BDE (Strandberg et al. 2001). One reason for this pattern in biological samples is that the less brominated congeners are reported to be very bioaccumulative, possibly more so than PCBs, and have been found to bioconcentrate in carp to more than 10,000 times higher than ambient levels (World Health Organization 1994b). In contrast, the more brominated congeners are not believed to bioaccumulate due to their high molecular mass (World Health Organization 1994b).

**Table 18: Commercial formulations of fire retardant PBDEs. Data source: (World Health Organization 1994b).**

Congener group	# of isomers	Formulation			
		Tetra-BDE <sup>2</sup>	Penta-BDE	Octa-BDE	Deca-BDE
Mono-BDEs	3				
Di-BDEs	12				
Tri-BDEs	24		0 – 1%		
Tetra-BDEs	42	41 - 41.7%	24 – 38%		
Penta-BDEs	46	44.4 – 45%	50 – 62%		
Hexa-BDEs	42	6 - 7%	4 – 8%	10 – 12%	
Hepta-BDEs	24			43 – 44%	
Octa-BDEs	12			31 – 35%	
Nona-BDEs	3			9 – 11%	0.3 – 3%
Deca-BDE	1			0 – 1%	97 – 98%
PBDE <sup>1</sup>		7.6%			

<sup>1</sup> Unknown structure.

<sup>2</sup> No longer commercially available.

There is considerable debate as to whether highly brominated congeners could be debrominating either in the environment or within biota (Renner 2000c). There is little evidence either way, though the very high persistence of all the PBDE congeners suggests that debromination is not significant (World Health Organization 1994b). Another contributing factor to the pattern of congeners in the environment is the greater airborne transportation potential of the more volatile (less brominated) congeners which would preferentially deposit them in locations far from sources (Ikonomou et al. 2000).

It is unclear at what stage PBDEs are released from the plastics and furniture foams that they are added to. The PBDEs are not covalently bonded to the plastics (as TBBPA is) but are mixed into the material and so are more easily released by leaching or volatilization. Some studies suggest that volatilization is the major source of PBDEs (Renner 2000c after Danish Environmental Protection Agency 1999). This is supported by the data showing them in significant amounts in air sampling near the Great Lakes (Strandberg et al. 2001), as well as in very remote locations such as Alert, NWT and Duai, Siberia (Renner 2000c). Treated sewage sludge applied to land in the U.S. contains high levels of PBDEs in a congener profile resembling that of penta-BDE (Hale et al. 2001). These authors noted that polyurethane foam (which uses penta-BDE) degraded into small particles very quickly when exposed to summer conditions. The penta-BDE may also be released during foam manufacture. Methylene chloride is commonly used to enhance foam expansion. This same chemical is highly effective at solubilizing PBDEs and has actually been used to extract PBDEs from environmental samples (Hale et al. 2001).

There is very little information on the toxicity of the various PBDE congeners (Renner 2000c), although the less brominated congeners (e.g. tetra and penta) are thought to be more toxic than the more brominated octa- and deca-BDE (Renner 2000c). Studies show that tetra- and penta-BDE are endocrine disruptors that affect the thyroid system (de Boer et al. 2000). If this is correct, the lower brominated congeners are of greatest concern: they are the most bioaccumulative, the most easily dispersed through atmospheric

processes, and the most toxic of the PBDEs. As of 1999, while North America was consuming 51% of world's total PBDE production, it was consuming 98% of the world's penta-BDE formulation (Renner 2000a).

### 12.2.2 Alkylphenol Ethoxylates (APEOs)

Alkylphenol ethoxylates (APEOs) are non-ionic surfactants consisting of a branched-chain alkylphenol with an attached ethoxylate chain. Nonylphenol ethoxylates (NP $n$ EO) make up 80% of the world market with octylphenol ethoxylates (OP $n$ EO) making up most of the remaining 20% (Warhurst 1995). Annual global production of APEOs is estimated at 500 kt for use in detergents (industrial and domestic), paints, pesticides, textiles, personal care products (especially shampoos), plastic, metal working fluids, petroleum recovery products, and pulp mill surfactants (Government of Canada et al. 2001; Warhurst 1995; Renner 1997). In the Georgia Basin, the use of NP $n$ EO as a reportable pesticide product totalled 3,660 kg in 1999 and OP $n$ EO a further 2,116 kg (ENKON Environmental Limited 2001). These figures do not include APEO use in pesticides as an inert ingredient since inerts are not reported. Furthermore, based on knowledge of APEO use and monitoring of effluents, the main contribution of APEOs to the Georgia Basin (and elsewhere) is via treated and untreated sewage (ENKON Environmental Limited 1999; Renner 1997; Hale et al. 2000). The discovery in 1984 that APEO breakdown products are more toxic to aquatic organisms than the parent compounds led to APEO bans and restrictions in Europe. Much of northern Europe had voluntary bans on APEO use in household cleaning products by 1995 with industrial restriction set to follow in 2000 (Renner 1997).

Early studies showed that APEOs were sufficiently broken down by sewage treatment and that concentrations in effluent would be negligible. However, Swiss researchers demonstrated in the 1980s that the surfactants were being transformed into much more toxic compounds during biodegradation. These degradation products have also proven to be more persistent, more lipophilic, more estrogenic and less water soluble than their parent compounds (Government of Canada et al. 2001; Renner 1997; Shang et al. 1999; Bennie 1999). The toxicity has been shown to increase with decreasing chain length (Servos 1999). Nonylphenol (NP) and octylphenol (OP) are the products of the removal of all the ethoxylate units from NP $n$ EO and OP $n$ EO respectively [The length of the ethoxylate chain varies between 1 and 50 ethoxy units, the number of which is denoted in the place of the  $n$  in the shortened name (e.g. NP $_9$ EO is a nonylphenol with a 9 unit ethoxy chain)]. Both NP and OP are acutely toxic to fish (LC $_{50}$  from 0.017 to 3 mg/L depending on species (Servos 1999)), and NP is roughly 10 times more toxic than its ethoxylates. Concentrations of NP in sewage have been found to increase 15-fold during anaerobic digestion (Renner 1997 after Giger et al. 1987). Anaerobic degradation removes ethoxy groups from the ethoxylate chain. Aerobic biodegradation removes an ethoxy group and then forms nonylphenol ethoxycarboxylates (NP $n$ ECs) which are essentially NP $n$ EOs with carboxylate groups on the end of the ethoxy chains. The study of a sewage treatment plant in Canada found that almost 80% of the APEOs in the final effluent were in the carboxylate form. The carboxylate derivatives are thought to be less toxic than the ethoxylates, but like all the APEOs they are believed to be endocrine disruptors.

The endocrine disrupting properties of 4-nonylphenol are well known. This compound has shown to be estrogenic in fish (Harris et al. 2001; Jobling and Sumpter 1993). The threshold for vitellogenin induction (an endocrine disruption indicator) in fish is 0.010 mg/L for NP and 0.003 mg/L for OP. Although APEOs degrade readily under some conditions, studies of NPnEOs in cores from the Georgia Basin suggest that little degradation occurs once they are in the sediments. The estimated half-life of NPnEO in these sediments is greater than 60 years (Shang et al. 1999). Persistence has not been high in other studies under different conditions (Maguire 1999). Although the main source of APEOs is sewage effluent (ENKON Environmental Limited 1999), they are also released by pulp mill effluent (Lee and Peart 1999), have been found in sewage sludge applied to land (Renner 1997; Bennie 1999), and can be found in stormwater and industrial effluents (Hale et al. 2000). Nonylphenol ethoxylates were declared toxic under the *Canadian Environmental Protection Act* (CEPA) on June 23, 2001, which will require control instrument development within 24 months (Grant and Ross 2002).

### 12.2.3 Fluorinated Organic Compounds (FOCs)

Fluoro-organic chemicals have one or more of the carbon-hydrogen (C-H) bonds replaced by a carbon-fluorine (C-F) bond. The C-F bond is thermodynamically one of the strongest known bonds making these compounds potentially more persistent than PCBs. Perfluorinated chemicals are those in which all of the C-H bonds are replaced by C-F bonds. These chemicals are excellent surfactants as they reduce surface tension better than other surfactants and are both hydrophobic and lipophobic (Renner 2001). Being lipophobic they were not expected to bioaccumulate like lipophilic POPs, but they bind strongly to blood proteins and accumulate in the liver and gall bladder (Renner 2001). These chemicals also have low vapour pressures, but a recent study has shown that they are found in wildlife throughout the world including non-industrialised areas (Giesy and Kannan 2001). This study looked at four perfluorinated chemicals and found that only one, perfluorooctane sulfonate (PFOS), was found at significant levels in most samples. A study of nonindustrially exposed humans also found PFOS to be the dominant FOC in blood serum (Hansen et al. 2001). Although PFOSs are found everywhere, Kannan et al. (2001) found the highest levels in organisms from inland waters near urban centres. It was postulated that consumer products were the primary source and so exposures were highest near direct discharge sites. Bioaccumulation of PFOSs has been shown to range from 6,300 to 125,000 times higher than ambient levels (Renner 2002b).

PFOS and related chemicals have been manufactured since the 1950s but their use has been increasing steadily since the 1970s (Giesy and Kannan 2001). Currently they are used for a number of purposes including surfactants, refrigerants, and components of pharmaceuticals, fire retardants, lubricants, paper coatings, cosmetics, pesticides, and shampoos (Renner 2001; Renner 2000b; Giesy and Kannan 2001). These compounds have been used in surface treatments such as the 3M product Scotchgard™. In the year 2000, some of the major uses included: 2.2 million kg for surface treatments (including around 1.1 million kg on carpet, clothing and upholstery protection), 0.6 million kg for a variety of specialized industrial uses such as fire-fighting foams, and ~1.2 million kg to protect paper products (Renner 2001).

PFOS is widely distributed, persistent and bioaccumulative, but it has not clearly been shown to be toxic. Too few studies have been done to quantify toxicity but PFOS compounds have been shown to affect cell to cell communication, membrane transport, and the process of energy generation (Giesy and Kannan 2001). In May 2000, evidence of the presence of the PFOS compounds throughout the environment prompted 3M to voluntarily remove Scotchgard™ and a few other PFOS containing products from the market (Renner 2000b). The reporting of pulp and paper mill and pesticide surfactant formulations are not required which makes it impossible to utilise local use levels as a guideline for prioritization. No direct measurements of PFOS in the B.C. environment have been made. However, based on the variety of common uses for PFOSs and the urbanization of the lower mainland, their presence is almost certain and likely to be at levels of concern.

#### ***12.2.4 Polychlorinated Naphthalenes (PCNs)***

Polychlorinated naphthalenes (PCNs) are often listed as “new” POPs because they have not been extensively studied and presented analytical difficulties until 1975 (Yamashita et al. 2000a). However, they are generally thought of as “legacy” POPs because they were first manufactured in the 1920s and continued to be manufactured until the mid-1980s (Alcock et al. 1999), they are structurally similar to PCBs, dioxins and furans (Blankenship et al. 2000), and they are used for similar purposes. PCNs are persistent, bioaccumulative, and some congeners have dioxin-like toxic activity similar in magnitude to some PCBs (Hanberg et al. 1990). Although no longer commercially produced, PCNs are still used in electrical equipment today; they are released by municipal waste incineration, chlor-alkali plants, leaching from landfill sites; and they occur as impurities in PCB mixtures. Global production was estimated at 150,000 t in 1998 (Villeneuve et al. 2000 after Falandysz 1998). Sediment cores from Tokyo Bay indicate that PCN levels have peaked and are now decreasing (Yamashita et al. 2000a; Yamashita et al. 2000b). Data for the Lower Mainland and Strait of Georgia is unavailable, but concentrations are unlikely to be rising.

#### ***12.2.5 Polychlorinated Terphenyls (PCTs)***

Polychlorinated terphenyls (PCTs) are also similar in structure and attributes to PCBs. They are a more complex group because they have three aromatic rings instead of two and so the number of possible congeners increases to 8,149 versus 209 for PCBs (Grant and Ross 2002; Hale et al. 1990). PCTs were manufactured during a similar period to PCBs, 1955-1980, totalling about 60,000 metric tonnes which is 15-20 fold less than PCBs. Concentrations in environmental samples tend to reflect this production ratio. They are considered “new” POPs because the ability to detect them in samples has improved greatly in recent years. PCTs have many similar properties to PCBs and were also used in electronic equipment, and as lubricants, sealants, hydraulic fluids, plasticizers, paints, and flame retardants (de Boer 2000; Hale et al. 1990). PCTs are bioaccumulative, persistent, and are believed to have similar mechanisms of toxicity to PCBs; however quantification has been made difficult by the contamination of PCT mixtures with PCBs (de Boer 2000). Ecotoxicity may be slightly lower due to the higher molecular sizes than PCBs (Paasivirta 1998; Paasivirta 2001). As with PCNs, data for



the Lower Mainland and Strait of Georgia are unavailable but due to the lack of current production, environmental levels are unlikely to be rising.

#### **12.2.6 Polychlorinated *n*-Alkanes (PCAs)**

Polychlorinated *n*-alkanes (PCAs) are also called chlorinated paraffins (CPs) and polychlorinated paraffins (PCPs). As with PCNs, these chlorinated contaminants are considered “new” because difficulties with analyses have prevented significant research until recently (Tomy et al. 1999; Government of Canada et al. 1993a; Paasivirta 2001). PCAs are chlorinated derivatives of *n*-alkanes with carbon chain lengths from C<sub>10</sub> to C<sub>30</sub> and a chlorine content ranging from 30 to 70% by weight. They are divided up into three groups: short chain (C<sub>10</sub>-C<sub>13</sub>), medium chain (C<sub>14</sub>-C<sub>17</sub>) and long chain (C<sub>20</sub>-C<sub>30</sub>). Short chain PCAs are used primarily as lubricants, flame retardants, and sealants; medium chain PCAs as plasticizers (e.g. in PVC) and extreme temperature/pressure additives in metalworking fluids; and long chain PCAs are used in paints and as lubricants and flame retardants (Government of Canada et al. 1993a; Alcock et al. 1999; Stern and Tomy 2000; Farrar 2000). Commercial production of PCAs began around 1930 (Alcock et al. 1999) and continues today although global production is reported to have declined since the 1980s (Muir et al. 2000). However, other sources quote a 1985 and 1993 global production estimate at 300 kt/yr (Tomy et al. 1999; Alcock et al. 1999). Canadian consumption was estimated at 3.5-5 kt/yr in 1990 (Government of Canada et al. 1993a).

Short chain PCAs have similar physical properties to POPs such as PCBs and toxaphene and are thus the main environmental concern (Tomy et al. 1999; Government of Canada et al. 1993a; Muir et al. 2000). Medium and long chain PCAs are not well understood but are believed to be less volatile and less toxic than short chain PCAs (Government of Canada et al. 1993a; Muir et al. 2000). Short chain PCAs have been found throughout the environment and a recent study of Arctic lake sediments suggests that long range atmospheric transport is a significant distribution mechanism (Tomy et al. 1999). The same study showed that the highest levels were likely related to local sources (urban/industrial) and that lake sediments showed a peak concentration from the early 1980s to the 1990s. The short chain PCAs are acutely toxic to fish although toxicity quantification is made difficult by the fact that fish seem to show effects many days after exposure making traditional 48 or 96 hour LC<sub>50</sub> data irrelevant (Government of Canada et al. 1993a). Concern over short chain PCAs is high enough that they are considered Track 1 Priority Toxic Substances under CEPA and are also on the USEPA Toxic Release Inventory. Internationally they have been proposed as candidate POPs under the United Nations Environment Programme POPs Convention. The Convention for the Protection of the Marine Environment of the North-East Atlantic voted in favour of a prohibition of releases to the sea. Also, they were among the first group of chemicals to be considered as Priority Chemicals for Risk Assessment under European Union Regulation 793/93 (Farrar 2000).

#### **12.2.7 Phthalate Esters**

Phthalate esters represent a large class of widely used industrial compounds consisting of dialkyl or alkyl aryl esters of 1,2-benzenedicarboxylic acid. These compounds are commonly used as softeners in plastics, but they are also found in perfumes, hairsprays,

lubricants, pesticides, and wood finishes (Myers 2002a; Government of Canada et al. 1993c; Government of Canada et al. 1994a; Government of Canada et al. 1994b; Environment Canada and Health Canada 2000). Phthalate releases to the environment are primarily into the atmosphere during the manufacture of plastics and during incomplete combustion of plastics, but they also leech from plastics after manufacture. They have been detected in water, air, soil and biota in Canada, despite being considered non-persistent except in anaerobic sediments and soils (Government of Canada et al. 1993c; Government of Canada et al. 1994a; Government of Canada et al. 1994b; Environment Canada and Health Canada 2000). Phthalates are not thought to be highly bioaccumulative though they are reported to be fat soluble (Warhurst 1999). Current literature repeatedly states that little is known about these substances because of difficulties with analytical procedures. Phthalates are ubiquitous in rubber and plastics and are also present in laboratory reagents, solvents and supplies making it nearly impossible to take and analyse a sample without contaminating it. Even the air in a lab is likely to contain phthalates volatilized from the equipment (Government of Canada et al. 1993c; Government of Canada et al. 1994a; Government of Canada et al. 1994b; Environment Canada and Health Canada 2000; Staples et al. 2000).

Under the CEPA, four phthalates have been assessed under the Priority Substances List Assessment Reports (Government of Canada et al. 1993c; Government of Canada et al. 1994a; Government of Canada et al. 1994b; Environment Canada and Health Canada 2000). All reports have concluded that there is insufficient data to make a full assessment. Three of the reports concluded that, based on available data, phthalates are not being released into the Canadian environment in sufficient quantities to pose a danger to the environment. These reports covered dibutyl phthalate (DBP, also di-*n*-butyl phthalate), di-*n*-octyl phthalate (DnOP), and butylbenzylphthalate (BBP). The fourth report covered di(2-ethylhexyl) phthalate (DEHP, also bis(2-ethylhexyl) phthalate) and did not make any assessment of environmental risk due to lack of data. In addition to their toxicity, phthalate esters are of environmental concern since many of them are confirmed or suspected endocrine disruptors (Myers 2002a; Jobling et al. 1995).

**12.2.7.1 Dibutyl phthalate:** As of the report (1994), DBP was no longer produced in Canada, but about 540 tonnes/year used to be imported, mainly for use as a plasticizer in polyvinyl emulsions. The volume of DBP imported as additives to plastic products is not known. The amount transported into Canada by the atmosphere is not known but the Great Lakes were estimated to receive a total atmospheric deposition of 48 tonnes/year in 1981 (Government of Canada et al. 1994b; Eisenreich et al. 1981). A Lowest Observed Effect Level (LOEL) for rainbow trout was reported as 0.19 mg/L (Government of Canada et al. 1994b; Ward and Boeri 1991) and 96 hour LC<sub>50</sub>s for other fish species ranged from 0.35 to 0.6 mg/L (Mayer and Ellersieck 1986). Most of the reported environmental concentrations in Canada are from industrial and sewage effluents and air samples in Ontario (Government of Canada et al. 1994b).

**12.2.7.2 Di-*n*-octyl phthalate:** As of the report (1993), DnOP was no longer produced in Canada, but about 1 tonne had been used in Canada each year. It has been detected in industrial fluid effluents, sewage sludge, and occasionally in

surface waters and sediments (Government of Canada et al. 1993c). Very little information exists on the specific toxicity of DnOP.

**12.2.7.3 Butylbenzylphthalate:** is not manufactured in Canada but about 4 kt were imported into Canada in 1996. BBP has been detected in a variety of effluents across Canada including industrial effluents in B.C. in 1985 (Environment Canada and Health Canada 2000). BBP has been detected in biota from marine and estuarine organisms in B.C., up to 1470 ng/g wet weight in a Boundary Bay butter sole, though most samples were <100 ng/g (Various sources in Environment Canada and Health Canada 2000). The 96 hour acute toxicity of BBP for fish ranged from 0.51 to >1 mg/L.

**12.2.7.4 Di(2-ethylhexyl) phthalate:** DEHP had an estimated production of 5kt/y in 1991 with an additional 5kt imported (Government of Canada et al. 1993c). DEHP accounts for well over 50% of the total use of phthalate plasticizers with a world wide production of roughly 1,000 kt/year (World Health Organization 1992). Atmospheric transport of DEHP into Canada is likely significant since environmental release of this phthalate from industry in the U.S. was estimated at 500 tonnes in 1989 and 97% of that went into the atmosphere (Government of Canada et al. 1994a; TRI89 1991). DEHP has been detected in municipal wastewater from Vancouver and estuary sediments in the Fraser River (Rogers et al. 1986; Rogers and Hall 1987). Very little toxicological data exists for DEHP. A 96 hour LC<sub>50</sub> with rainbow trout was reported as >0.32 mg/L (Government of Canada et al. 1994a after Chemical Manufacturers Association 1990).

Other phthalates mentioned in the literature but not specific to Canada include dimethyl and diethyl phthalate (DMP, DEP) (Staples et al. 2000), di-*n*-pentyl phthalate (DPP) (Myers 2002a), and monoethylhexylphthalate (MEHP) (Warhurst 1999).

#### **12.2.8 Other “new” POPs**

A number of “new” POPs show up in the literature as being of global concern but there is little or no information about their use or presence in the British Columbia environment. There is often no information on their toxicity to aquatic biota. Some of these chemical classes are discussed in *The Handbook of Environmental Chemistry. Series 3: Anthropogenic Compounds. Volume 3K: New Types of Persistent Halogenated Compounds* edited by J. Paasivirta (2000), and other papers (Paasivirta 1998; Paasivirta 2001).



## 13 CONCLUSIONS

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Based on the available data it is not possible to determine at this time whether the recent change in Fraser River late-run sockeye salmon behaviour has been caused by exposure to any environmental contaminants. Factors including oceanographic conditions, disease, or local conditions such as river temperature may be wholly, or in part, to blame for the change in late-run sockeye behaviour. However, we remain concerned about a possible role for environmental contaminants. The increased use of a number of chemicals in the late-run sockeye salmon habitat in B.C. during the 1990s highlights the risk that contaminants may present to organisms inhabiting or frequenting the Fraser Basin. Considerable knowledge gaps exist in terms of contaminant characterization in B.C. salmonids and possible effects on their health. For the purposes of this review, we categorized contaminants as high, medium, low, or unknown risk factors in the observed behaviour change should contaminants be contributing to the sockeye behaviour change. The unknown risk category contains chemicals for which there is currently not enough information to make any kind of assessment of either their presence in B.C. waters or their capability of affecting sockeye salmon behaviour. Although several chemicals have been highlighted below as part of this scoping exercise, this list should not be considered in isolation nor as all-inclusive.

### 13.1 HIGH RISK

- **Pesticides:** The use of certain pesticides are clearly increasing in the Fraser Basin. These pesticides were prioritized using degree and consistency of increase in reported sales. At the top of this list are metam sodium, formaldehyde, and chlorothalonil.
- **Wood Preservatives:** The wood preservatives creosote, CCA, ACA, and ACZA show increasing use during the 1990s and are known to have lethal and sublethal effects on fish.
- **Some “new” POPs:**
  - **Polybrominated diphenylethers:** PBDEs are increasing exponentially in the environment. Two forms of PBDEs, the tetra- and penta-BDE, are believed to be the most toxic, and have been found to possess endocrine disrupting properties. North America consumes 98% of the world’s penta-BDE production, largely for use as a flame retardant. PBDEs are found in treated wastewater and sewage sludge but are ubiquitous in the environment due to atmospheric transport.
  - **Phthalate esters:** These are the most commonly used family of plasticizers. As such they are also ubiquitous and most likely increasing in the environment (difficulties in analysis have made data scarce). In addition to their toxicity, many phthalate esters are confirmed or suspected endocrine disruptors.
  - **Alkylphenol ethoxylates:** APEOs represent a widely-used family of chemical surfactants found in municipal wastewaters, pulp mill effluent, urban runoff,

and as inert ingredients in many pesticides. Nonylphenol ethoxylate and its degradation products have received the most attention for their endocrine disruption capabilities. Nonylphenol has been implicated in population level impacts on the health of Atlantic salmon stocks. Recent work has shown that secondary treatment of effluent containing APEOs only serves to break them down into their more toxic and endocrine disruptive degradation products.

### 13.2 MEDIUM RISK

- **Triclopyr:** This pesticide was increasingly used in the forestry sector during the 1990s. Increases appear to be contemporaneous with the changes in sockeye behaviour, although no causal link is evident. Data limitations preclude an accurate assessment at this time. Further research into watershed specific sources and sublethal toxicity to fish are needed.
- **Sodium ferrocyanide:** By 1995, B.C. forest fire fighters switched from using a variety of fire retardants to almost exclusive use of FireTrol<sup>®</sup> 931. This product contains sodium ferrocyanide, which degrades to cyanide in the presence of sunlight. There may be a link between the use of this fire retardant and the sockeye behaviour change but, as for triclopyr, no causal link is evident. Data that are specific to the Fraser Basin would allow a more accurate assessment.
- **“Legacy” POPs:** PCBs, dioxins, furans and OC pesticides are generally decreasing in the North American environment. However, evidence suggests that salmon are exposed to “legacy” POPs in the North Pacific Ocean that migrate from countries where controls have not yet been implemented (e.g. parts of Asia). Exposure to these persistent compounds therefore represents an unknown risk to salmonids, meriting attention.
- **Polycyclic aromatic hydrocarbons:** Some sources of PAHs are increasing. These include the use of the wood preservative creosote, vehicular traffic and other sources that relate to population growth. A number of PAHs are toxic, and a few are suspected of being endocrine disruptors.
- **Heavy metals:** Increasing population pressure is leading to increased inputs of heavy metals into the environment. Urban runoff and storm drains are major sources, along with recycled sewage sludge and WWTP effluent that has not received secondary or tertiary treatment. Some of the metals identified from these sources include copper, chromium, lead, zinc, nickel, and arsenic. There has also been a significant increase in the use of four metal-bearing pesticides: the wood preservatives ACZA and CCA, and the pesticides cupric hydroxide and copper oxychloride.
- **Antisapstain chemicals:** The use of DDAC, IPBC, and “borax” based anti-sapstain chemicals in B.C. was fairly consistent during the 1990s. These chemicals are known to be toxic to fish. They are not considered higher priority because their use has not shown a clear and consistent increase during the 1990s and the implementation of “best practices” procedures is believed to have

reduced spills and runoff contamination from lumber treatment facilities by 99%.

### 13.3 LOW RISK

- **Tributyltin:** This known toxin and endocrine disruptor has been used in boat and ship hull paints to prevent the growth of encrusting organisms. After significant environmental effects were noted, its use was restricted to ocean-going vessels, and it is likely to be banned completely. Since the restrictions were imposed, effects have declined in North America.
- **Antisapstain chemicals:** The use of sodium carbonate, and TCMTB declined in B.C. during the 1990s and the use of Azacozole was low and remained so. This makes these contaminants low risk for involvement in the sockeye behaviour change. Furthermore, the implementation of “best practices” procedures is believed to have reduced spills and runoff contamination from lumber treatment facilities by 99%.
- Some “new” POPs:
  - **Polychlorinated naphthalenes:** Manufacture of PCNs is reported to have ceased in the mid 1980s. Like PCBs, they are still present in some ‘closed applications’ such as electrical equipment. Data for current levels and trends in B.C. is lacking but the cessation of manufacturing indicates that environmental concentrations are not likely to be rising.
  - **Polychlorinated terphenyls:** As with PCNs, the manufacture of PCTs is reported to have ceased in the 1980s as well. Current data for these compounds in B.C. is also lacking. Thus, despite their being persistent, bioaccumulative, and toxic, PCTs are unlikely to have increasing concentrations in salmon habitat.

### 13.4 UNKNOWN RISK

- **Pharmaceutical and personal care product chemicals:** These contaminants have been largely ignored in comparison to other contaminants. However, increasing evidence of effects, such as endocrine disruption, highlight concerns about these products. No data was available on levels of these contaminants in the B.C. environment and very little information was available on effects. Recent data from the U.S. suggests that these compounds are common in the river waters of highly populated areas.
- **Inert pesticide ingredients:** These ingredients do not have to be listed on pesticide labels, even though many of them are toxic (e.g. APEOs). No data were found on which chemicals are used in this manner in B.C. and in what volume they are entering the B.C. environment. The increase in pesticide use suggests that inert ingredient use is also increasing.
- **Pesticide degradation products:** The half-lives of pesticides are often calculated but rarely are the products of degradation listed, nor are they included

in toxicity tests. A few examples are known where pesticide ingredients can degrade to chemicals that are more toxic and often more persistent (e.g. APEOs, metam sodium, and dazomet).

- **Some “new” POPs:**

- **Polychlorinated *n*-alkanes:** The production of PCAs is declining, but their persistence is such that they could still be accumulating in the aquatic food chain. Current data are needed to assess this possibility.
- **Fluorinated organic compounds:** This family of surfactants has been found in wildlife throughout the world. Of these compounds, perfluorooctane sulfonate (PFOS) is by far the most commonly found and seems to be ubiquitous in the environment, probably as a result of atmospheric transport. Its highest concentrations are found near industrial and urban centres. It is persistent and bioaccumulative, but its toxicity is debated. Based on its discovery in wildlife, one of the major commercial products containing PFOSs (Scotchgard™) was voluntarily withdrawn (decision in May 2000). This compound is likely to be present in the B.C. environment but there are no local measurements.

### 13.5 SUMMARY OF INFORMATION GAPS

- There are no data on contaminant concentrations or types present in Fraser River late-run sockeye salmon. We only have indirect evidence for exposure (e.g. pesticide survey).
- The use of several pesticides and forestry chemicals are increasing but no data exist on their presence in specific areas used by late-run sockeye or on their concentrations in the tissues of sockeye salmon.
- The environmental levels of some “new” POPs are increasing world-wide but remain largely uncharacterized in sockeye habitat and tissues.
- Some “legacy” POPs have been found at high concentrations in biota in B.C. despite regulations and source controls. These contaminants are likely present in all stages of the sockeye life cycle but a comprehensive assessment of exposure is lacking.
- Sockeye salmon have large habitat requirements and anthropogenic effects may be pronounced in some of these areas. The extent of chemical impacts are unknown (WWTP effluent, agricultural runoff and EDCs).
- Toxicity literature notes that certain early life stages of fish tend to be sensitive to many contaminants. Specific information on late-run sockeye salmon and key contaminants of concern is lacking.



- There exists little toxicological information on sublethal effects of many contaminant classes, despite the fact that subtle alterations can lead to serious, population level impacts.

*Considerable research gaps exist but there is clear reason for concern about contaminants and their potential risk to the health and viability of late-run sockeye salmon.*



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## APPENDIX 1

### Selected Pesticide Notes

#### Organochlorine Pesticides

##### Chlorothalonil

- **Use:** Nonsystemic fungicide used on tomatoes, potatoes, lawns, turf, trees, fruits, and roses. Second most widely used agricultural fungicide in the U.S.
- **Acute toxicity:**  $LC_{50}$  for rainbow trout from 0.01 to 0.076 mg/L but quoted as high as 0.25 mg/L
- **Sublethal effects:** 0.002 mg/L caused gill damage and anaemia in rainbow trout.
- **Bioconcentration factor:** up to 940 times in rainbow trout.
- **Persistence:** soil half-life of 1 to 2 months; water < 2 hours.
- **Water solubility:** 0.6 mg/L at 25°C.
- Primary metabolite is 4-hydroxy-2,5,6-trichloroisophthalonitrile which is about 30 times more toxic and is more persistent and mobile than chlorothalonil.
- Found in air and precipitation samples in the great lakes and in Arctic fog.

##### Quintozene (also pentachloronitrobenzene, PCNB)

- **Use:** Dominantly a fungicide for seed and soil treatments, also a herbicide and slime inhibitor in industrial waters.
- **Acute toxicity:**  $LC_{50}$  for rainbow trout 0.55 mg/L though another found no fatalities at 1.2 mg/L.
- **Bioconcentration factor:** varies from 200-1200 in fish.
- **Persistence:** Soil half life varies from several weeks to almost 2 years; water ~ 2 days. Another reported soil 3 weeks to over 1 year; water 1.8 to 5 days.
- **Water solubility:** practically insoluble in water: 0.44 mg/Litre at 20 °C.
- Readily adsorbs to sediments, suspended sediments and biota in water.
- Degrades to pentachloroaniline (PCA).
- Expected be persistent in sewage sludge.

#### Organophosphate Pesticides

##### Diazinon

- **Use:** insecticide that is most widely used for domestic purposes (home, lawn and garden). In the U.S. it is estimated that domestic use is roughly 5 times that of agricultural use.
- **Acute toxicity:** AChE inhibitor (neurotoxin) with 96 hour  $LC_{50}$  for rainbow trout of 0.090 mg/L. Another reported  $LC_{50}$  is 2.6 to 3.2 mg/L. Some evidence that saltwater fish are more susceptible.
- **Sublethal effects:** genetic damage at 0.00016 mg/L in the central mudminnow, reduced olfactory stimulated response of male atlantic salmon to the smell of female urine at 0.0003 mg/L, disrupted anti-predator and homing behaviour via olfactory disruption as low as 0.001 mg/L.
- **Bioconcentration factor:** 18-300 though it was reported at 2300 for gills and 1850 for liver.
- **Persistence:** 2-4 weeks in soil; up to 6 months in water.
- **Water solubility:** 40 mg/L at 20°C.
- Reported as a common contaminant in the effluent of wastewater treatment plants in the U.S. and most commonly detected insecticide in urban streams in the U.S.
- Subject of a report suggesting domestic diazinon use in the U.S. northwest is affecting Pacific salmon.
- USEPA announced elimination of all indoor uses and began phase-out of lawn and garden uses.

##### Terbufos

- **Use:** insecticide and nematicide used on corn, sugar beets, etc. Primarily formulated as granules and applied to seed furrow.

- **Acute toxicity:** 96 hour  $LC_{50}$  from 0.008 to 0.0013 mg/L in rainbow trout .
- **Bioconcentration factor:** 680 times for bluegill sunfish.
- **Persistence:** 5 to 30 days in soil; 5 to 14 days in water.
- **Water solubility:** 5 mg/L.
- The major degradate is formaldehyde.

#### Fosetyl Aluminum

- **Use:** systemic fungicide used to control damping off and rot of plant roots, stem and fruit. Used on lawn and turf, various fruit trees, ginseng, asparagus, etc.
- **Acute toxicity:** Studies available to the USEPA suggest fosetyl aluminum is not a risk to fish.
- Very little information exists on this pesticide.

#### Glyphosate, Trimethylsulfonium salt

- All existing information on glyphosate refers to the isopropylamine salt form and occasionally the acid form. No information is available on this form of glyphosate. Toxicity is highly specific so the toxicity of other forms does not convey any information on the toxicity of this form.

### Carbamate Pesticides

#### Carbaryl

- **Use:** wide spectrum insecticide used to control over 100 species of insects on fruit trees, some crops, lawns, ornamentals, and on livestock and pets. One of the three most commonly used insecticides in the U.S.
- **Acute toxicity:**  $LC_{50}$  of 1.3 mg/L for rainbow trout.
- **Sublethal effects:** damage to gill, liver and kidney noted at <1 mg/L. At 0.01 mg/L fish had tremors, reduced development and vision abnormalities.
- **Bioconcentration factor:** 140-fold measured in fish.
- **Persistence:** 7 to 28 days in soil; roughly 10 days in water though highly variable.
- **Water solubility:** 40 mg/L at 30°C
- Primary breakdown product is 1-naphthol and is considered more toxic to some fish than the parent compound.

#### Propamocarb Hydrochloride

- **Use:** Specific fungicide used commonly on potatoes, turf and ornamentals.
- **Acute toxicity:** Although a carbamate, propamocarb does not inhibit AChE activity. 96 hour  $LC_{50}$  410-616 mg/L for rainbow trout.
- **Persistence:** 30 day half life in soil; up to 97% degraded in water after 35 days.
- **Water solubility:** 1005 g/L at pH 7.

### Inorganic Pesticides

#### Cupric Hydroxide and Copper Oxychloride

- No information was found on these specific compounds. It is assumed that their toxicity to fish would be due to the copper content so information on copper toxicity is included here:
- **Acute toxicity:** copper  $LC_{50}$  values of 0.026 to 0.034 mg/L for juvenile chinook salmon.
- Further information on copper in Wood Preservatives section.

#### Lime Sulphur or Calcium Polysulphide

- No information was found on these compounds. Toxicity information is given for sulphur below.

#### Sulphur

- **Use:** Non-systemic contact and protectant fungicide used on fruit, hops, vegetables, roses, etc., as well as on livestock.
- **Acute toxicity:** 96 hour  $LC_{50}$  > 180 mg/L for rainbow trout.
- **Persistence:** In one study after 2 years less than 30% of applied sulphur had leached from the soil. No data on persistence in water.
- **Water solubility:** practically insoluble in water.

## Miscellaneous Pesticides

### Metam Sodium

- **Use:** Dithiocarbamate soil fumigant used to kill nematodes, soil pathogens and weeds. 1997 USEPA estimates it to be the third most commonly used pesticide in the U.S. Furthermore, half the U.S. use is in the Pacific Northwest.
- **Acute toxicity:** Metam sodium itself is not particularly toxic and, in fact, is not the actual fumigant chemical. Shortly after application, Metam sodium breaks down to methylisothiocyanate (MITC) which is the true active ingredient.
- **Sublethal effects:** Possible hormone disruptor.

### Mancozeb

- **Use:** Mancozeb is an ethylene bis-dithiocarbamate used to as a fungicide on fruit, vegetable, and field crops, and as a seed treatment.
- **Acute toxicity:** 48 hour LC<sub>50</sub> for rainbow trout is 2.2 mg/L.
- **Persistence:** half life of 1 to 7 days in soil; 1 to 2 days in water.
- **Water solubility:** 6 mg/L.
- Degrades to ethylenethiourea (ETU) which has caused goiter, birth defects and cancer in animals.

### Paraquat

- **Use:** A quaternary nitrogen herbicide widely used for broadleaf weed control. Has been used as an aquatic herbicide.
- **Acute toxicity:** 96 hour LC<sub>50</sub> for rainbow trout is 32 mg/L and for brown trout is 13 mg/L.
- **Persistence:** soil half life > 1000 days; water half life 13 hours to 23 weeks.
- **Water solubility:** 700,000 mg/L at 20°C.

### Iprodione

- **Use:** A dicarboximide fungicide used to control a wide variety of crop diseases on vegetables, fruits, ornamentals, etc.
- **Acute toxicity:** LC<sub>50</sub> of 6.7 mg/L for rainbow trout.
- **Bioconcentration factor:** 50 to 360 in carp.
- **Persistence:** half life in soil from 7 to 60 days; breaks down rapidly in water.
- **Water solubility:** 13 mg/L at 20°C.

### Linuron

- **Use:** A phenyl urea herbicide used to control broadleaf and grassy weeds on both crop and non-crop sites.
- **Acute toxicity:** LC<sub>50</sub> for trout is 16 mg/L.
- **Sublethal effects:** liver and kidney damage at 0.030 mg/L.
- **Persistence:** half life in soil 30 to 150 days ; not readily broken down in water.
- **Water solubility:** 81 mg/L at 25°C.
- Concentrations of 1.1 and 2.8 mg/L have been detected in Canadian surface waters. Has endocrine disrupting capabilities.

### Diuron

- **Use:** A phenyl urea herbicide used to control a wide variety of broadleaf and grassy weeds as well as moss. It is used on both non-crop and crop sites such as fruit.
- **Acute toxicity:** 96 hour LC<sub>50</sub> for rainbow trout is 3.5 mg/L.
- **Sublethal effects:** Goldfish showed effects at 0.005 mg/L including olfaction effects. Higher concentrations had an attractive effect.
- **Persistence:** soil half lives from 1 month to 1 year; relatively stable in water.
- **Water solubility:** 42 mg/L at 25°C.

### Pendimethalin

- **Use:** A selective herbicide used to control most annual grasses and certain broadleaf weeds in field crops.
- **Acute toxicity:** 96 hour LC<sub>50</sub> for rainbow trout is 0.138 mg/L.
- **Bioconcentration factor:** 5100 in whole fish.
- **Persistence:** field half life of 40 days.
- **Water solubility:** 0.3 mg/L at 20°C.

### Formaldehyde

- **Use:** unknown.
- **Acute toxicity:** between 10 and 100 mg/L for fish.
- **Bioconcentration factor:** expected to significantly bioaccumulate.
- **Persistence:** Low persistence expected.
- **Water solubility:** Infinite.

### 2,4-D Amine

- **Use:** A chlorinated phenoxy herbicide used to control many types of broadleaf weeds. Widely used for agriculture, pasture and rangeland, forest management, home and garden. The most widely used herbicide in the world.
- **Acute toxicity:** Toxicity is highly dependent on the form of 2,4-D used: ester, acid, amine, or salt. The available information related mostly to the ester forms. Almost no information was available for 2,4-D amine. Ester toxicity: LC<sub>50</sub> 0.7 mg/L for rainbow trout.

### Napropamide

- No data was found on this pesticide active ingredient.

### Picloram

- **Use:** Systemic pyridine herbicide used to control woody plants and a range of broad-leaved weeds.
- **Acute toxicity:** 96 hour LC<sub>50</sub> for rainbow trout is 19.3 mg/L.
- **Sublethal effects:** 0.5 mg/L caused degenerative changes in liver and gills of yearling coho.
- **Bioconcentration factor:** not expected to accumulate in aquatic organisms.
- **Persistence:** soil half life 20 to 300 days; water half life 2.6 days however, it has been found in surface waters 35 months after helicopter application.
- **Water solubility:** 430 mg/L at 25°C.
- Contaminated with the endocrine disrupting organochlorine POP hexachlorobenzene.
- Highly mobile in soil.

### Triclopyr

- **Use:** A pyridine selective systemic herbicide used for control of woody and broadleaf plants along rights of way, in forest management, and on industrial lands, parklands and grass lands.
- **Acute toxicity:** ester formulation has a 96 hour LC<sub>50</sub> of 0.74 mg/L for rainbow trout.
- **Sublethal effects:** On rainbow trout noted as low as 0.6 mg/L with avoidance reactions at 19.2 mg/L.
- **Bioconcentration factor:** 1.08 for bluegill sunfish.
- **Persistence:** soil half life from 30 to 90 days; water half life from 2.8 to 83.4 hours.
- **Water solubility:** 440 mg/L at 25°C.
- Discussed in detail in the Forestry Chemicals section.
- Degrades to trichloropyridinol (TCP) which is more persistent and roughly as toxic as the ester form.

### Metalaxyl

- **Use:** xylylanaline fungicide used as a soil and seed treatment.
- **Acute toxicity:** very low, 96 hour LC<sub>50</sub> of > 100 mg/L.
- **Persistence:** soil half life 7 to 170 days; water half life < 4 weeks.
- **Water solubility:** 7,100 mg/L at 20°C.