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Persistent Organic Pollutants in White-Tailed Deer (*Odocoileus virginianus)* Near a Magnesium Smelter: Spatial Distribution and Human Health Risk Assessment

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Persistent Organic Pollutants in White-Tailed Deer (*Odocoileus virginianus*) Near a Magnesium Smelter: Spatial Distribution and Human Health Risk Assessment

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Abstract

A magnesium refining facility in Quebec was a known point source of persistent organic pollutants namely polychlorinated biphenyls, dioxins and furans, and hexachlorobenzene. Contaminants concentrations were measured in the fat tissue of local white-tailed deer with the assistance of the local community and hunters. Concentrations in the deer from 1999, one year before the smelter opened, were compared with deer from 2002. Results showed a significant increase in PCBs from 1999 to 2002, and total PCB concentrations showed significant decreases with distance from the smelter. Many of the mid-range PCB homologues that bioconcentrate sharply in deer showed similar relationships. ∑coplanar PCBs and Cytochrome P450 1A expression in liver also showed a significant inverse relationship with distance in 2002. Results of a human health risk assessment indicated that the number of deer meal portions required to exceed safe consumption levels for PCDD/Fs and coplanar PCBs increased with the distance from the smelter.

Résumé

Une fonderie de magnésium à Québec était une source ponctuelle connue de polluants organiques persistants, particulièrement les biphényles polychlorés, les dioxines/furannes, et les hexachlorobenzènes. Avec l'aide de la communauté et des chasseurs locals, la concentration des contaminants dans le tissu graisseux du Cerf de Virginie local a été mesurée. Les niveaux de contaminants dans les cerfs de 1999, un an avant l'ouverture de la fonderie, ont été comparés avec ceux de 2002. Les résultats ont démontré une augmentation substantielle de la concentration des BPCs de 1999 à 2002, et les ΣBPCs, ont démontré une diminution substantielle en s'éloignant de la fonderie. De plus, les BPCs coplanaires et l'expression du cytochrome P450 1A dans le foie du cerf, ont aussi démontré

une relation inverse significative avec la distance chez les cerfs de 2002. Pour déterminer le risque que pose la consommation de la viande de cerfs de la région à la population humaine, les niveaux de contaminants ont été comparés aux indications de consommation de l'Organisation mondiale de la santé (OMS) pour les PCDD/Fs et les composés semblables aux dioxines (BPCs coplanaires). Selon les résultats, le nombre de portion de viande nécessaire pour dépasser les limites de consommation sûres pour les PCDD/Fs et les BPCs coplanaires augmente avec la distance de la fonderie.

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1.0 Introduction

1.1 Research Objectives

The main objective of this study was to determine whether or not a smelter located in Danville, Quebec, Canada (Magnola Metallurgy Incorporated) is a source of persistent organic pollutants (POPs), namely polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxin/furans (PCDD/Fs), and hexachlorobenzene (HCB) to the surrounding environment. This was investigated by measuring concentrations in local white-tailed deer *Odocoileus virginianus* which accumulate these compounds by consuming vegetation contaminated via atmospheric deposition from the smelter. Research addressing the contamination of food webs as a result of local contamination has been identified as a "knowledge gap" by the Northern Contaminants Program and this study will contribute novel information on the distribution of these chemicals in this area (CACAR II, 2003).

Two groups of deer were analyzed: those captured before the smelter opened as a pre-impact control (deer from 1999), and two years after the smelter began operations (deer from 2002). Differences in concentrations of emission (PCBs, HCB) and non-emission products between the two groups of deer were examined in conjunction with factors such as distance from the smelter and deer age.

It was hypothesized that the smelter was a source of contaminants to the locality. To test this, I predicted that significant differences in emission products between deer from 1999 and 2002 would be observed, and no difference would be seen for other organochlorine compounds not emitted by the smelter. I also predicted that concentrations of emission products would decline with distance from the smelter in the 2002 deer only. The relationship between deer age and contaminant concentrations was investigated as ancillary evidence to the central hypothesis.

An additional objective was to determine whether or not the smelter was emitting PCBs, PCDD/Fs and HCB in quantities that would compromise the health of the local human population. The community surrounding the smelter is a very popular hunting area and venison is often a staple of local diets. Standardized dietary consumption guidelines were applied to contaminant levels measured in the deer to evaluate whether people in different age groups (toddlers, children, and adults) are at risk of adverse health effects as consumers of the game.

1.2 The Smelter: Background Information

The present study identifies a smelter that is emitting PCBs, HCB, and PCDD/Fs. Magnola Metallurgy Incorporated located in Danville, Quebec opened in the year 2000 and ceased operations in March of 2003 due to decreased magnesium prices attributed to the rise in magnesium exports from China. While it was operational, Magnola was one of largest magnesium refining facilities in the world. The chemical properties of magnesium, such as strength, conductivity, low density, and ability to withstand high temperatures, render it useful for a number of applications including aluminum alloying, die-casting and desulphurising. Die-casting for the automobile industry is the second and fastest growing application for magnesium, and use in handheld electronic devices and computing are additional areas projected for future growth (Forrest and Burstow 2004).

Magnola employed a new process whereby magnesium was recovered from mine tailings from past asbestos mining operations (Hatch 1997). Magnesium is extracted through an acid leaching process producing brine (a magnesium chloride solution), which is purified and dried to a granular form of magnesium chloride. This is melted into an electrolyte, treated in a chlorination process, and converted to a metallic form through a molten salt electrolysis and finally tapped into ingots (Figure 1.1) (Hatch 1997). Chlorine gas is

produced as a by-product in the electrolysis and chlorination processes and although most of it is recycled, some quantities react with carbon impurities on the graphite electrodes in the electrolytic cells, producing organochlorine compounds (Hatch 1997, BAPE 1998). The electroysis chambers are the primary source of organochlorines, accounting for approximately 65% of the total production while 20% are generated in the chlorination chambers (BAPE 1998). These are released in a gaseous form and are vented from the facility. The remaining 15% of organochlorines are volatilized from an open-air tailings lagoon where processing wastes (such as leaching residues) are deposited. Sludge produced from the treatment of chlorine for its re-use contains organochlorines as well, which are collected and treated off-site.

Prior to the opening of the smelter the forecasted breakdown of organochlorines to be released into the atmosphere were as follows: 34% hexachlorobenzenes, 13% decachlorobiphenyls, 0.004% polychlorinated dibenzo-p-dioxins and 0.5% polychlorinated dibenzofurans, and the remaining 52% chlorobenzenes, chlorophenol, and octachlorostyrene (BAPE 1998). These forecasts were made anticipating that the smelter would operate at full capacity; however this was not the case for the actual emission tests conducted while the smelter was operational. Magnesium production was lower than the smelter's full capacity of 58,000 tonnes per year; Magnola produced 9,339 tonnes in 2001 and 25,000 tonnes in 2002, which was 16% and 43% of its full capacity, respectively (Hatch 1997).

Measured emissions of PCBs and CBs in 2001 and 2002 were lower than those forecasted by Noranda in 1997 (Table 1.1). Additional tests in 2002 measuring ambient air concentrations in close proximity to the facility showed that levels were within normal background air concentrations and below acceptable limits defined by the Quebec government for dermal contact and inhalation. An important consideration, however, is the

bioaccumulation of contaminants in food chains and the associated long terms effects from the release of the chemicals into the environment.

Alarm was raised over PCDD/F emissions measured from the smelter in 2002 (1.7-5.2g/year) that were above the forecasted emissions for that year (0.09g/year), and were much higher than total emissions measured in 2001 (0.04gTEQ/year) (Table 1.1, Appendix 1.1). The electrolysis chambers were the primary source of PCDD/Fs. Based on these releases, the smelter contributed approximately 3.8% of the national average of PCDD/F emissions in 2002, and was Canada's fifth largest source of dioxins and furans (Table 1.2) (Environment Canada 2004, Environmental Defense and CELA 2004).

1.3 Persistent Organic Pollutants

1.3.1 Polychlorinated Biphenyls

Polychlorinated biphenyls (PCBs) are banned industrial chemical products but there is no legislation preventing their release as unintended by-products of industrial processes (Ritter et al. 1995, de March et al. 1998). Due to their desirable chemical properties such as low chemical reactivity, resistance to degradation, low flammability, high heat capacity, and insulation, PCBs were widely produced for use in electrical transformers and capacitors, hydraulic fluids and lubricants, plasticizers, and synthetic resins for rubbers and asphalts (US EPA and EC 2000). Monsanto was the primary manufacturer of PCBs in the United States between 1929 and 1977 and an estimated 40,000 tonnes were imported to Canada. Sixty percent of all PCBs in Canada currently exist on-land in dumps and landfills for storage and disposal, and in use primarily in electrical equipment (CCREM 1986). Tanabe (1985) estimated that of the total PCB world production, a similar quantity (65%) to that reported in Canada also remain in storage and in use, with an additional 31% dispersed into the environment (12% in terrestrial and coastal, 19% in the open ocean), and only 4%

incinerated and degraded. Such a great quantity of land-stocked PCBs poses concern for their future dispersal in the environment (Tanabe 1988).

PCBs are halogenated hydrocarbons comprised of a biphenyl molecule in which hydrogen atoms are substituted by chlorine (Figure 1.2). There are 209 PCB congeners grouped according to the varying degrees of chlorine substitution on the biphenyl rings, ranging from monochlorobiphenyl to decachlorobiphenyl (Matthews and Dedrick 1984, Mackay 1991, Ritter et al. 1995). The toxicity of PCBs varies with the number of chlorine atoms and according to their substitution positions.

The chemical properties of PCBs render it a highly toxic compound. With a wide range of volatilities, PCBs are distributed both at close and far range from sources. The mid-range PCBs are semi-volatile (vapor pressure 0.01 - 0.1 Pa) and travel from low to high latitudes in a process known as the "grasshopper effect" whereby compounds are evaporated in warmer temperatures, transported in the atmosphere and subsequently re-deposited by condensation in colder regions (Wania and Mackay 1996, Blais et al. 1998, Wania and Mackay 1998). The more highly chlorinated PCBs are less volatile, with vapor pressures ranging between 0.001 and 0.1 Pa, and these have a tendency to accumulate at mid-latitudes. The lower-chlorinated PCBs are relatively involatile (vapor pressure < 0.001 Pa), are most likely to be deposited in close range to their source but do have the potential for long-range transport because they partition appreciably into the atmosphere due to their hydrophobicity (Schwartzenbach et al. 1993, Ritter et al. 1995, Simonich and Hites 1995, Davidson 2002). PCBs persist in the environment for long periods of time, with half-lives ranging from three weeks to two years in air, two to six years in water, and two to six years in soil and sediment.

More highly chlorinated PCBs are recalcitrant to biotransformation and subsequent elimination (Matthews and Dedrick 1984). Several studies investigating elimination rates of

PCBs in marine mammals and fish have shown that PCB congeners with adjacent chlorine-substituted positions are not readily metabolized, in particular those with chlorinated *para* positions and adjacent chlorinated *para-meta* (known as *"non-ortho"*) positions (Figure 1.2) (Muir et al. 1988[1], Norstrom et al. 1988, Coristine et al. 1996). Studies reporting this include de Boer et al. (1994) who found that hexachlorobiphenyls and octachlorobiphenyls were not eliminated at all from eels in an 8-year study under natural conditions, similarly Porte and Albaiges (1993) found that chemical degradation in crustaceans and fishes was slowest for PCBs with 2,4,5 chlorine substitution. PCB metabolism also varies in different species, and studies have shown that mammals metabolize PCBs faster than birds, which in turn metabolize PCBs more rapidly than fish (Huntzinger, 1972). Metabolic rates vary even within the same species and this has been attributed to differences and seasonal variability in diet, fat content, age, sex, habitat location and body condition (Sipes et al. 1982, Norstrom et al. 1988).

The mid-range PCBs have a tendency to bioaccumulate and biomagnify in food chains. Migratory animals such as salmon and seabirds have been shown to concentrate these chemicals in the Arctic (Krümmel et al. 2003, Blais et al. 2005). Connell and Hawker (1988) developed a model describing the bioaccumulation patterns of organic compounds in relation to various chemical properties and used a bell-shaped curve to quantify the relationship between contaminant uptake and elimination and lipophilicity, as indicated by the octanol-water partition coefficient ($\log K_{ow}$). Experimentally, the ratio of uptake to elimination is described by a bioconcentration factor (BCF), which represents the extent to which compounds concentrate in animal tissue relative to their diet (Lorber et al. 1994, Newman and Unger 2003). Lower-chlorinated PCBs have low $\log K_{ow's}$ and do not bioaccumulate to a great extent, while the mid-range PCBs have high $\log K_{ow's}$ and high BCFs. $\log K_{ow's}$

continue to increase with the most highly chlorinated PCBs, such as nona- and deca-chlorobiphenyl, however, the BCFs level off and decrease. (Figure 1.3, Table 1.3) (Schwarzenbach et al.1993). The Flory-Huggins Theory explains this discrepancy by relating solubility to molecular size, where the bioaccumulation of mid-range PCBs is primarily controlled by membrane diffusional processes, and this is impeded by the greater molecular size characterized by the most highly chlorinated PCBs (Chiou 1985, Connell and Hawker 1988, Newman and Unger 2003).

1.3.2 Coplanar PCBs

20 out of the 209 PCB congeners with a non-*ortho* substitution pattern are known as coplanar PCBs (nPCBs). Three of these (PCB-77, -126, -169) have a planar configuration similar to that of PCDD/Fs, with chlorine atoms at both *para* and 2 or more *meta* positions. Coplanar PCBs induce toxicity by binding to the cytosolic Ah receptor protein, a mechanism common to PCDD/Fs, and they exhibit dioxin-like toxic effects (Ahlborg et al. 1993, Feeley and Grant 1993, Schwarzenbach et al. 1993). Coplanar PCBs are evaluated with a Toxic Equivalency Factor (TEF), which is a ratio assigned to coplanar PCBs based on their toxicity relative to tetrachlorodibenzo-p-dioxin 2,3,7,8-TCDD. The World Health Organization has set universally accepted TEFs of 0.005, 0.1 and 0.01 for PCB-77, -126, and –169, respectively, PCB-126 being the most toxic (Ahlborg et al. 1993). Coplanar PCBs have exhibited slow uptake and clearance in lower organisms; PCB-77 being the most easily metabolized in mammals, and PCB-126 the least (Tanabe et al. 1987, Kannan et al. 1989). For example, in a study quantifying PCBs in whales from the contaminated St-Lawrence river system, PCB-126 was found to be present in the greatest proportions compared to the other coplanar PCBs (Muir et al. 1996). Similarly Tanabe et al. (1987)

observed greater proportions of PCB-126 and -169 than PCB-77 in marine and terrestrial mammals.

1.3.3 Organochlorine Pesticides

Hexachlorobenzene, octachlorostyrene, and chlorophenol were other organochlorine compounds emitted from the smelter as a by-product of magnesium production, the former of which was measured in this study. Prior to being banned in the late 1970's hexachlorobenzene was used as a fungicide primarily on grains. Currently it is released from the manufacturing of chlorinated solvents, rubber tires and pesticides and is volatilized from pesticide application (Ritter et al. 1995, de March et al. 1998). HCB is volatile and can bioaccumulate because it is lipophilic, as indicated in its relatively high octanol-water partition coefficient (K_{ow}5.5) (Table 1.3) (MacKay et al. 1992c). Other POPs that were measured but are not emission products from the smelter include Mirex, DDT, Dieldrin, Aldrin and HCH. These were primarily used as insecticides and their use is presently restricted (de March et al. 1998).

1.3.4 Dioxins and Furans

Polychlorinated dibenzo-p-dioxin/furans (PCDD/Fs) are unintended by-products of chlorinated industrial processes. Prior to the ban of PCBs and other organic chemicals, PCDD/Fs were formed as impurities in the manufacture of organochlorines, such as commercial PCB preparations, and also in various pesticides. Presently, sources include fuel and waste combustion processes, metal refining, wood preservative pentachlorophenol, and pulp and paper mills; the latter of which has been reduced worldwide with the use of non-chlorinated bleaching agents (de March et al. 1998).

Dioxins and furans are an extremely toxic class of organochlorine compounds. Dioxins are comprised of 2 benzene rings joined by two oxygen atoms and furans are joined

with one oxygen atom (Figure 1.2) (ATSDR 1998). There are 210 PCDD/F isomers in total with homologue groups ranging from mono- to octa-, designated according to the degree of chlorination. Dioxins and furans are persistent in the environment and bioaccumulate in the food chain due to their lipophilicity (Table 1.4). 2,3,7,8 TCDD (tetrachlorodibenzo -*p*-dioxin) is the most toxic anthropogenic chemical known. 2,3,7,8-substituted PCDD/F isomers bioaccumulate to the greatest extent. For example, Wu et al. (2001) found 2,3,7,8-PCDD/Fs to be the most prominent of PCDD/F congeners in an aquatic-avian food chain. Several dioxins and furans exert a number of common toxic responses similar to those observed for 2,3,7,8 TCDD and seventeen PCDD/Fs are assigned TEFs (toxic equivalency factors) to represent their degree of toxicity (Hites 1990, Van den Berg et al. 1998).

In this study, organic pollutants enter the terrestrial food chain from vegetation. The octanol-air partition coefficient (K_{oa}) is a measure of a chemicals' tendency for deposition on terrestrial surfaces such as plants and soil (Wania and Mackay 1996). This ratio increases with decreasing volatility and increasing levels of chlorination (Table 1.4). PCDD/Fs are relatively involatile, and the range of volatilies in this group of chemicals influence their distribution in the environment. Studies have suggested that the more highly chlorinated PCDD/Fs are more persistent because they have been found to occur in greater concentrations than the less chlorinated PCDD/Fs in soil and sediment (Hites 1990, ASDTR 1998). The highly-chlorinated congeners are less volatile and are subject to particle-bound deposition, rendering them more efficiently scavenged from the air into environmental media compared to the more volatile, lower-chlorinated PCDD/Fs which exist to a greater extent in the vapor phase. The lower-chlorinated PCDD/Fs also tend to remain in the atmosphere for longer periods of time where they are subject to photodegradation.

1.4 Bioaccumulation in the Terrestrial Food Chain

The present study addresses the possible bioaccumulation of PCBs, HCB and PCDD/Fs in deer through an air - vegetation - herbivore contaminant pathway. Vegetation is a sizable sink for lipophilic organic pollutants from the atmosphere (Simonich and Hites 1995). A mass balance model of PAH (polycyclic aromatic hydrocarbons) transfer between air, water, vegetation, soil and sediment developed by Simonich and Hites (1994) showed the extent to which vegetation acts as a sink for semi-volatile organic compounds, reporting that 44% of local PAH emissions in the northeastern US were taken up by vegetation annually. Similarly Matzner (1984) found that vegetation litter accounted for 30-70% of the PAH deposition onto spruce and beech forest floors in Germany.

Compounds that are lipophilic and recalcitrant, such as the mid-range PCBs, bioaccumulate to higher trophic levels in the food chain while the more easily metabolized, lower-chlorinated PCBs generally do not and are detected for the most part at lower trophic levels (Thomas et al. 1992). Total PCB concentrations increased by 6.5-fold from plants to lemmings in the vicinity of a Distant Early Warning (DEW line) radar site in the NWT (Reimer et al. 1993a). Elkin (1994) found total PCB and HCB concentrations to be greater at higher trophic levels in a lichen-wolf-caribou food chain in the NWT. It was predominantly the middle homologues (penta- through octa-CB) that bioaccumulated in the caribou, while the lower chlorinated PCBs were more prevalent in the lichen. Similarly Muir et al. (1988[1]) found a predominance of penta-, hexa-, and hepta-chlorobiphenyls in animals at higher trophic levels of an arctic marine food chain (seal and polar bear), while tri- and tetra-chlorobiphenyls were present only in species at lower trophic levels (fish). Larsson et al. (1990) examined a short food pathway consisting of the herbivorous vole and the carnivorous shrew, and comparatively found that lower-chlorinated PCB congeners were

present in greater proportions in the voles, while the mid-range PCB congeners were more prevalent in the predatory shrew.

1.5 Spatial Trends of Close-Range Contamination

Because organochlorines are highly regulated, studies of close-range spatial patterns are conducted in the vicinity of active point sources or sites where chemicals have been previously discarded or stored. Several years of monitoring following a spill at a PCB disposal centre in Swan Hills Alberta showed that the facility was a local source of contamination. Deer sampled from within 20km of the site had significantly greater levels of PCBs and PCDD/Fs than those beyond 20km, and concentrations decreased significantly with distance from the source (Gabos et al. 1998). An inverse relationship between total PCB concentration in vegetation and distance from the source was documented by Blais et al. (2003), where a predominance of highly chlorinated PCB congeners was found in spruce needles within 3km of the incinerator.

A well - known source of PCBs is the abandoned DEW (Distant Early Warning) line radar sites spanning across Greenland and the North American Arctic. In the 1990's, many of these sites in the Canadian Arctic were converted to new radar stations under the Northern Warning System (NWS) and various environmental risk assessments were conducted and continue to-date (de March et al. 1998, Braune et al. 1999). A recent study of one of the facilities on the shore of Saglek Bay Labrador found that caribou on-site had substantially greater PCB concentrations than those sampled 6km away (Gregor et al. 2003). In the same region Pier et al (2003) showed evidence of local contamination based on matching congener patterns in plants, soil and sediment samples extending up to 27km from the source, and also found that total PCB concentrations in samples within 3km of the site were 48 times greater than those further away. PCB levels in marine sediments near this location were inversely

related to distance from the source, and concentrations in the immediate vicinity of the site ranged between 1000-5000ng/g, dropped to 100ng/g at 2.5km, and decreased by a large margin to less than 1ng/g in remote locations (10-25km from the site) (Kuzyuk, 2000). An earlier study by Bright et al. (1995a) conducted surveys of soils and plants in the vicinity of 24 of the radar stations across the Canadian Arctic. PCBs were present in greater concentrations at samples taken within 10km of a site as compared to remote locations (greater than 20km from a site) and PCB congener signatures in soils within 10km of a site correlated with those from the actual radar sites, while signatures from remote sites did not.

1.6 Deer Ecology

Deer were selected for biomonitoring in this study and have been selected for biomonitoring of contaminants from point and regional sources in many other studies (Hernandez et al. 1985, Falandysz and Kannan 1992, Gabos et al. 1998, Zasadowski et al. 2003, Naso et al. 2004). Their role in the food chain makes for a well-defined contaminant pathway and their small home ranges (Table 1.5) are particularly useful for quantifying localized contaminant sources (Holm 1993, Elkin and Bethke 1995, Froslie et al. 2001, Naso et al. 2004). Deer also provide information on human exposure to chemicals because they are consumed by hunters and their families. In addition, large sample sizes are available because a great number of deer are shot each year (Holm 1993).

White-tailed deer *Odocoileus virginianus* in the Asbestos region serve as a good indicator for local contamination due to the limited size of their range, which ranged between 0.25- 25km^2, based on studies of this species in North America and Europe (Table 1.5). The summer home range sizes are very small in comparison to the spatial scale of this study (over 2800km^2). Summer home range sizes of other deer populations were considered for home-

range approximation of the deer in this study because they feed mostly in the summer and fall when preferred forage is more readily available, and they must build up fat reserves for the winter when they feed less in order to conserve energy (Mautz 1978). In addition, contaminant levels in deer tissue are typically lower in the late summer and fall when deer are building up fat reserves for the winter, and are greatest in the spring after fat stores have been depleted over the winter (Mautz 1978, Holm 1993).

Rouleau et al. (2002) reported a mean summer home range of 0.67km^2 for a rural, non-migratory deer population in a study area covering 100 km^2 in the foothills of the Appalachian Mountains, just 100km southeast of Montreal. This study also reported a mean summer home range of 1.09km^2 in a forest deer population occupying the more northerly Bas-Saint Laurent study area covering 240km^2, located approximately 200km east of Quebec City. The deer in this study are similar to the former deer population (non-migratory rural deer) due to characteristics of the landscape and the less remote northerly location.

Lesage et al. (2000) also conducted a study in the Bas-Saint Laurent study area, and reported a distance range of 9.7-24.6 km between winter and summer home ranges, which were 1.3km^2 and 24.4km^2, respectively. This summer home range size was greater in comparison to most deer populations in North America (Table 1.5) and this may have been a result of food shortages associated with a severe winter. However, these ranges and migratory distances lie within the boundaries of the study area at hand, and are well within the area designated as "near" (<5km) to the smelter which encompasses approximately 78.5 km^2.

1.7 Risk Assessment

In numerous animal studies, persistent organic pollutants have been shown to induce negative effects in the hepatic system (porphyria), alter the endocrine system by changing

thyroid horomone levels, and suppress the immune system and cause related ailments such as thymic atrophy (ATSDR 1998, de Wit et al. 2002). Reproductive effects in wildlife are well documented, for example Reijenders (1986) showed that reproductive failure in seals from the Wadden Sea in the Netherlands was related to the feeding of fish from a PCB polluted area. Similarly, ingestion of fish with high PCB loads from polluted Lake Michigan was thought to be the cause of reproductive failure in minks, and follow-up laboratory experiments have established that low oral PCB doses have a similar effect (Aulerich et al. 1971, Aulerich and Ringer 1977). Neurological and developmental effects from prenatal exposure have been documented. In studies where mothers were consumers of contaminated fish from Lake Michigan, high cord serum levels were associated with smaller birth size and neurobehavioral alterations in newborns, reduced gestation age, and poor visual recognition and short-term memory in four-year olds (Jacobson 1990 et al., Jacobson et al. 1992, Lonky et al. 1996). Transplacental exposure to background PCB levels in North Carolina was linked to poor performance on tests indicative of psychomotor development in infants up to twelve months old (Gladen et al.1988, Tilson et al. 1990). A recent study that measured the effects of contaminants on Inuit infants in several Nunavik communities was consistent with the US studies in finding cognitive defects in infants of mothers with elevated blood cord plasma PCB levels (Muckle et al. 2004). Immediate symptoms of acute exposure include ocular and dermal affects, such as chloroacne, and such effects were observed after a widespread PCB food poisoning incident in Japan, and an accidental PCDD/F release in Seveso, Italy (Kuratsune et al. 1972, ATSDR 1998). PCBs are classified as "probable human carcinogens" and PCDD/Fs are known carcinogens in lab animals (de Wit et al. 2002). Knox et al (2005) found a direct link between childhood leukemia and close proximity (within 1km) to dioxin point-sources is in the UK. In epidemiological research it is difficult to draw

direct correlations between adverse health effects and specific chemicals due the wide range and latency period of the effects, confounding factors that also influence health (for example: smoking, history of heart disease), and a combination of chemicals in the environment that may cause synergistic effects.

Safe levels of dietary consumption for humans is evaluated by the TDI (tolerable daily intake) which stipulates the quantity of chemicals, commonly expressed in grams, per kilogram bodyweight per day, that can be safely consumed over a lifetime without causing adverse health effects (Feeley and Grant 1993). TDI's are calculated based on clinical tests on animals used to determine a no-adverse-effect level (NOAEL) or a lowest-adverse effect-level (LOAEL) for particular endpoints, and body burdens of the different species tested are used to scale the doses (Rolaf van Leeuwen 2000, WHO 2000). A safety factor is applied to account for uncertainties in the TDI calculation, which arise from differences in susceptibilities to endpoints between humans and the species tested, interindividual toxicokinetic variation among humans, and differences in half-lives of the chemicals (Rolaf van Leeuwen 2000, WHO 2000).

This study applies the World Health Organization and Health Canada's TDI for PCBs and dioxins and furans. Recently Health Canada revised its TDI for PCBs to a more restrictive limit, from 1ug kg^{-1} bw day^{-1} to 0.13 ug kg^{-1} bw day^{-1}, and for PCDD/Fs and coplanar PCBs, from 10pg TEQ kg^{-1} bw day^{-1} to a more conservative monthly limit of 70 pg TEQ kg^{-1} bw $month^{-1}$. The latter value lies in the mid-range of the WHO TDI of 1-4 pg TEQ kg^{-1} bw day^{-1} (JEFCA 2002). There have been inconsistencies between international consumption guidelines, and their re-evaluation is on-going. A study by Hites et al (2004) made safe meal advisories for salmon based on US guidelines and found that the FDA had an estimated cutoff that was 40 times higher than what the EPA determined to be safe for sale in

supermarkets. In 2002 a discrepancy between WHO and the Health Canada TDI for PCDD/Fs translated to a 10-fold difference in the recommended number of salmon meals that could be safely consumed (Health Canada 2001, Easton et al. 2002).

The WHO TDI specifies a range (1-4 pg TEQ kg^{-1} bw day^{-1}) where the upper number is considered the maximum intake on a temporary basis, and the lower value is a target TDI for restricting human intake, leaving room for interpretation on a case-by-case basis (WHO 1998, 2000). Some studies take a conservative approach, for example Easton et al. (2002) stipulated that consuming farmed salmon with coplanar PCB and PCDD/F levels above WHO's TDI lower-boundary value of 1 pg TEQ kg^{-1} bw day^{-1} would cause increased risk of adverse health effects. In contrast, a study of traditional foods hunted by Inuit people where PCB levels exceed the TDI recommended continued consumption because the nutritive benefits outweighed potential health risks (Kinloch et al.1992). A recent report by the Northern Contaminants Program stated that due to uncertainty in the TDI, exceeding it "does not necessarily mean that health problems will occur" (CACAR II, 2003). In many industrialized countries average daily intake of foodstuffs lies close to or exceeds safe levels. Studies in Europe have found foodstuffs with PCDD/Fs and coplanar PCBs exceeding the lower-boundary limit of the WHO TDI (1 pg TEQ kg^{-1} bw day^{-1}), and concluded that these levels were safe because they fell *within* the WHO range (Focant et al. 2002, Fernandez et al. 2004). In addition, subtle health effects which have been reported as a result of consumption of contaminated foods cannot solely implicate PCDD/Fs and coplanar PCBs (WHO 1998).

1.8 Biomarkers

The induction of cytochrome P450 liver enzymes (CYP 1A), more commonly known as mixed function oxidase enzymes (MFO's), is a well known biological response to pollutant exposure (Peakall and McBee 2001). The cytochrome P4501A1 family of liver

enzymes are induced by dioxins and furans, coplanar PCBs, and PAHs, and their catalytic activity was measured in this study using an EROD (ethoxyresorufin *O*- deethylase) bioassay, where enzyme activity was derived from the formation of resorufin from 7-ethoxyresorufin, a reaction catalyzed by EROD (Kennedy and Joes 1994, 1997).

MFO's are a gene family of hemeproteins that metabolize foreign compounds and endogenous substances via oxidation, thereby increasing water solubility and the rate of xenobiotic excretion. This mechanism protects vertebrates from certain pollutants, but upon exposure to high concentrations, MFOs can interfere with the metabolism of endogenous substances, affecting other biological processes in the body (de March et al. 1998). Enzymes are induced through the binding of xenobiotic substances to the aryl hydrocarbon receptor (AhR) in the cytoplasm, forming an AhR complex that enters the nucleus. Here, it reacts with a dioxin-responsive element (DRE) on DNA, inducing CYP (cytochrome P450) DNA transcription to CYP mRNA translation, and CYP protein formation, which is quantified in the EROD assay (Figure 1.4) (Feeley and Grant 1993, Hodson et al. 1998).

EROD activity has been used successfully as a biomarker of contaminant exposure in various species such as birds, fish, and marine and terrestrial mammals (de March et al. 1998). EROD activity was measured in beluga whales and polar bears from contaminated waters in the Canadian Arctic and correlated with body burden contaminant loads (White et al. 1994, Letcher et al. 1996). Nyman et al. (2000) found that EROD activity was 5-times greater in seals from polluted waters in contrast to less polluted waters. Shipp et al. (1998) reported a dose-dependent relationship in EROD activity in mink which were fed non- and PCB contaminated fish. In deer, EROD activity was induced for the first time in a study by Sivapathasundaram et al. (2003), and the study at hand further investigates this species as a biomarker of exposure.

Studies have also questioned the extent to which EROD is a legitimate index of biological response to contaminant exposure. Many studies use EROD activity as evidence of exposure to a particular contaminant; however, there are additional factors that have also been shown to affect induction (de Wit et al. 2002). Jorgensen et al. (1999) showed that diet affected CYP1A induction in Arctic charr in a controlled study where the fish were divided into four groups: fed and PCB-exposed, fed and not exposed, starved and PCB-exposed, starved and not exposed; the third being the only group with elevated EROD activity. Henriksen et al. (1998) found low EROD activity in glaucous gulls with high PCB body burdens, and stated that this trend was due to a low metabolic capacity for PCBs in this particular species. Similarly, in a study of fish from highly contaminated rivers in the Czeck Republic by Siroka et al. (2005), the highest levels of EROD did not scrictly coincide with the highest PCB concentrations in fish tissue and sediment. This was explained by the possibility of exposure to other AHR agonists, such as PAHs and TBT, and reduced sensitivity to CYP1A due to past contaminant exposure, as demonstrated by Brammell et al. (2004). In addition, hormonal factors have been shown to affect CYP1A induction, and this was shown in a study by Elskus et al. (2004) where estradiol suppressed CYP1A expression in rainbow trout. Interspecies and interindividual variability in EROD activity have been documented, the latter in herring gulls for example, and this is thought to be due to differences in toxicokinetics, and also polymorphisms in the CYP1A1 genes (Kennedy et al. 2003, van Duursen et al. 2005). As with any scientific method, confounding factors need to be considered, however EROD is widely used and considered a valid biomarker of contaminant exposure (Letcher et al. 1996).

Table 1.1 PCB, PCDD/F, and HCB emissions forecasted and reported from the smelter. Emission forecasts made prior to the smelter's opening in 2000 are contrasted with actual test results. Various tests are shown reporting emissions from the different sources within the smelter. Forecasts are based on production at full capacity and actual production was 16% and 43% of full capacity in 2001 and 2002 respectively.

Emissions reported in tests from different sources*	PCBs	PCDD/Fs TEQ	CB
Collecting reservoir [a]			
Forecasted 1997	1.3kg/year	20g/year	54kg/year
Measured 2001	0.29kg/year	0.18g/year	0.17kg/year
Measured 2002	0.22kg/year	0.11g/year	<0.2kg/year
Aerial Emissions [b]			
Forecasted 1997	3.02kg/year	0.09g/year	21.17kg/year
Measured 2001	1.18kg/year	0.04g/year[c]	9.1kg/year
Measured 2002	0.51kg/year	3.5g/year	16.99kg/year
Emissions from electrolysis chambers 2002[d]	0.3kg/year	3.0 g/year	8.69kg/year [e]
Ambient air concentrations 2002[f]	0.061 – 0.116g/m^3	0.002 – 0.052pg/m^3	<0.2 – 0.65 ng/m^3 [e]

[a] Emissions expressed in terms of volatilization from an open-air tailings lagoon where process wastes were disposed.
[b] Aerial Emissions measured in 2001 and 2002 and forecasted from 4 chimneys and one vent, expressed as a total from the following processing chambers: electrolysis, acid leaching, brine drying , casting, HCl synthesis, thermal quench chamber.
[c] Aerial Emissions do not include the emissions from the electrolysis chambers.
[d] Emissions measured solely from the electrolysis chamber, expressed as an average of 6 tests August-December 2002 conducted by the Quebec Ministry of the Environment.
[e] Hexachlorobenzenes.
[f] Tests averaged from four air sampling stations within 1km and north and northeast of Magnola.
**All tests were from Noranda's self-monitoring* (Noranda Inc. 2002, Hince, Noranda Inc., personal communication)

Table 1.2 PCDD/Fs released by Magnola in 2002 contrasted with Canada's top 10 polluters.

	PCDD/Fs g TEQ
Magnola Metallurgy Inc.	1.68 – 5.20[a]
Canada's total PCDD/F releases in 2002	92.42
Magnola PCDD/F production as a % of the national total emission	1.80 – 5.60
Canada's top 10 PCDD/F emitting facilities: average on-site releases	
1. City of Hamilton - SWARU Incinerator	10.3
2. Grand Falls-Windsor - Exploits Regional Solid Waste Disposal Site	8.01
3 Harbour Grace - Conception Bay North Incinerator Association	4.78
4 IPSCO Saskatchewan Inc. - Regina Plant Site	3.75
5 Métallurgie Magnola Inc.. Danville	3.59[b]
6 Town of Wabush - Incinerator	3.52
7 Wabash Alloys Mississauga	3.49
8 Town of Marystown NL- Waste Disposal Site Jean De Baie	3.26
9 Town of Holyrood NL - Incinerator	2.58
10 Town of Channel NL- Port aux Basques - Incinerator	2.56

[a] Range of emissions are reported from the electrolysis chambers, as measured by the Quebec Ministry of the Environment, August through November in 2002 (n=6). (Hince, Noranda Inc., personal communication).
[b] Average of values in (a)

Table 1.3 Chemical properties of PCBs and HCB.

	Molecular Weight (g/molecular)	Vapour Pressure[a] (Pa) at 25°C	Water Solubility(g/m^3)	Log K_{ow} at 25°C	H or K_{aw} Pa m^3/mol	Log K_{oa}	Mean half-life air	water	soil, sediment
PCBs									
Mono-CB	188.7	0.9 - 2.5	1.21 - 5.5	4.3 – 4.6	42.45-75.55[b]	-			
Di-CB	223.1	0.008 - 0.6	0.06 - 2.0	4.0 – 5.3	17-92.12[b]	7.67[c]	1 week	2 years	2 years
Tri-CB	257.5	0.003 - 0.22	0.015 - 0.4	5.5 – 5.9	24.3 – 92.2[b]	7.96[c]	3 weeks	6 years	6 years
Tetra-CB	292	0.002	0.0043 - 0.010	5.6 – 6.5	1.72-45.6[b]	8.74[c]	2 months	6 years	6 years
Penta-CB	326.4	0.0023 - 0.051	0.004 - 0.02	6.2 – 6.5	24.8– 151.4[b]	8.99[c]	2 months	6 years	6 years
Hexa-CB	360.9	0.0007 - 0.012	0.0004 - 0.0007	6.7 – 7.3	11.9-818[b]		8 months	6 years	6 years
Hepta-CB	395.3	0.00025	0.000045 -0.0002	6.7 – 7	5.4[b]		8 months	6 years	6 years
Octa-CB	429.8	0.0006	0.0002 - 0.0003	7.1	38.08[b]		2 years	6 years	6 years
Nona-CB	464.2	-	0.00018 -0.0012	7.2 – 8.16			2 years	6 years	6 years
Deca-CB	498.7	0.00003	0.000761 (g/m^3)	8.26	20.84[b]		6 years	6 years	6 years
HCB	284.8	0.2447	0.005	5.5	131	6.8-6.9[d]	2 years		6 years

All data obtained from Mackay et al. 1992a unless otherwise specified.
[a] Sub-cooled liquid vapor pressure ; [b] de March et al. 1998 ; [c] Harner and Mackay 1995 ; [d] McLachlan et al. 1995

Table 1.4 Chemical properties of PCDD/Fs.

Polychlorinated dibenzo-*p*- dioxins and Polychlorinated Dibenzofurans	Molecular Weight (g/molecular)	Vapour Pressure[a] (Pa) at 25°C	Water Solubility (mg/m^3)	Log K_{ow} at 25°C	H or K_{aw} Pa m^3/mol	Log K_{oa}	Mean air	half-life water	soil, sediment
Tetrachlorodibenzo-p-dioxin			0.0193 – 0.55	6.6 - 7.1	3.33	9.91 [b]	1 week	3 weeks	2 - 6years
Pentachlorodibenzo-p-dioxin	356.4	4.23 x10 $^{-6}$	0.118	7.4	0.255	11.37 [b]	3 weeks	3 weeks	2 - 6 years
Hexachlorodibenzo-p-dioxin	391.0	1.45 x10 $^{-6}$	0.00442	7.8	1.084	11.16 [b]	3 weeks	2 months	6 years
Heptachlorodibenzo-p-dioxin	425.2	1.77 x10 $^{-7}$	0.0024	8	1.273	11.29 [b]	3 weeks	2 months	6 years
Octachlorodibenzo-p-dioxin	460	9.53 x10 $^{-7}$	0.000074	8.2	0.684	11.76 [b]	3 weeks	8 months	6 years
Tetrachlorodibenzofuran	306	1.99 x10 $^{-4}$	0.419	6.1	1.461	9.33 [b]	1 week	3 weeks	2 - 6 years
Pentachlorodibenzofuran	340.42	1.72 x10 $^{-5}$	0.236	6.5	0.505	10.19 [b]	1 week	3 weeks	2 - 6 years
Hexachlorodibenzofuran	374.87	3.08 x10 $^{-6}$	0.00825	7	1.545	10.23 [b]	-	-	-
Heptachlorodibenzofuran	409.31	5.74 x10 $^{-7}$	0.00135	7.4	1.425	10.64 [b]	3 weeks	2 months	2 – 6 years
Octachlorodibenzofuran	443.76	1.01 x10 $^{-7}$	0.00116	8	0.191	12.11 [b]	3 weeks	8 months	6 years

All data obtained from Mackay et al. 1992b unless otherwise specified:
[a] Sub-cooled liquid vapor pressure ; [b] Mclachlan et al. 1995

Table 1.5 Mean summer home range sizes for white-tailed deer populations in North America and Europe.

Summer home range size (km^2)	Region	Reference
0.67	Quebec (100km SE of Montreal)	Rouleau et al. 2002
1.09	Quebec (Bas-St-Laurent region)	Rouleau et al. 2002
24.4	Quebec (Bas-St-Laurent region: Lac Temiscouta and Pohenegamook)	Lesage et al. 2000
2.25	New York (Adirondacks)	Tierson et al. 1985
2.25	New Brunswick, Nova Scotia	Drolet 1978
3.19	Northern Minnesota	Nelson and Mech 1981, 1987

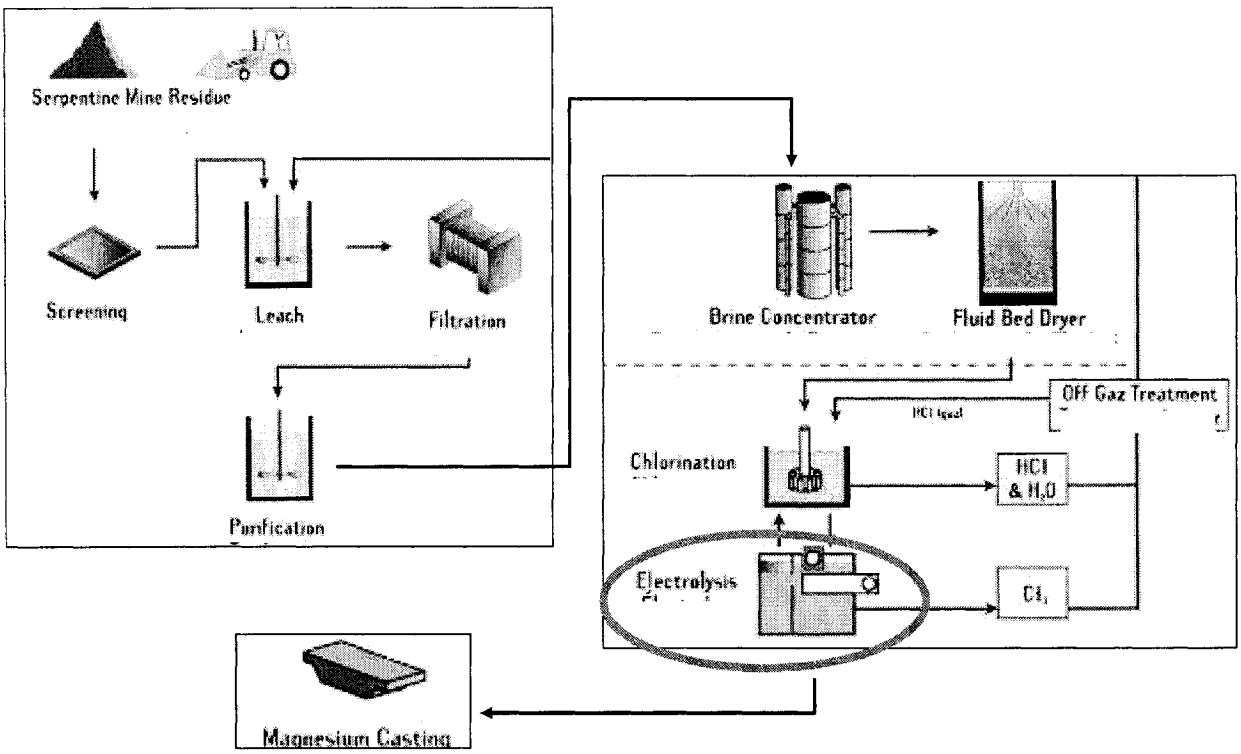
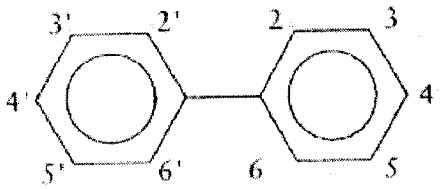
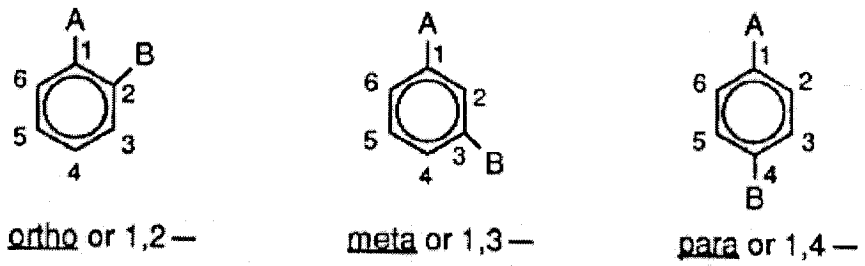


Figure 1.1 Magnesium production flow chart.

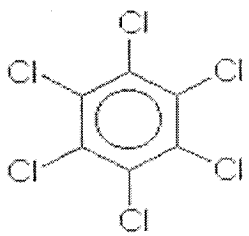
(Habashi, F. 1993)



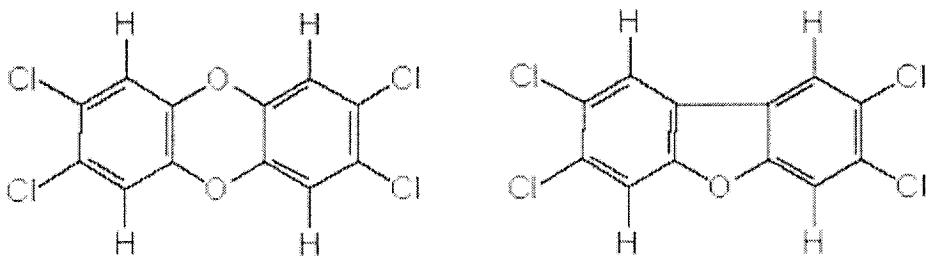
PCB



PCB Nomenclature: *ortho-*, *meta-* and *para*-Substitutions



HCB



PCDD and PCDF

Figure 1.2 Chemical structures and nomenclature of PCBs, HCB, and PCDD/Fs.

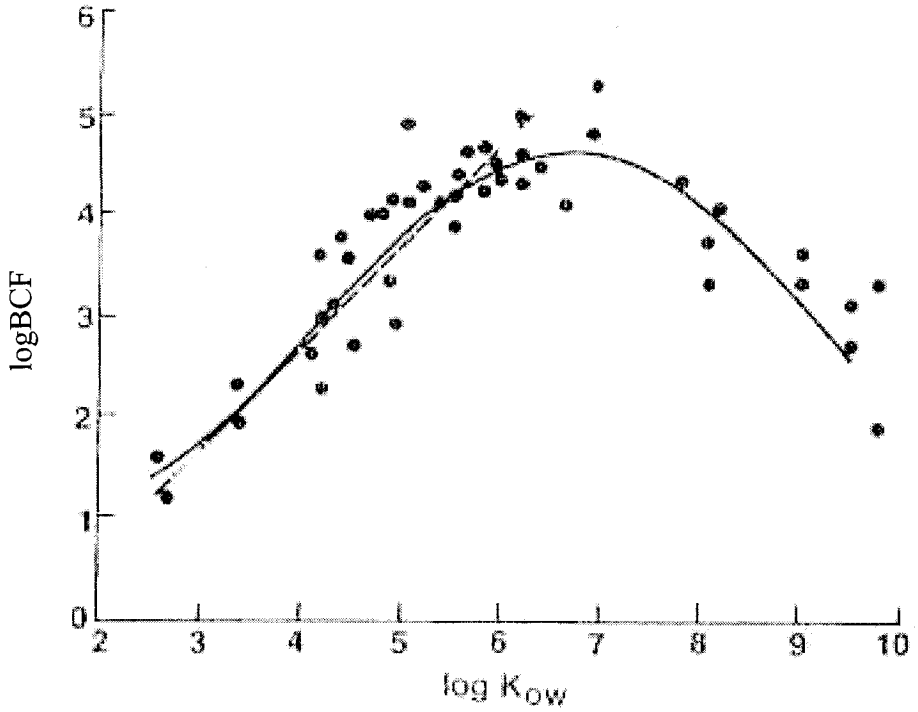


Figure 1.3 The relationship of bioconcentration (logBCF) factors to the octanol-water partition coefficients ($logK_{ow}$) for organic compounds.

(Connell and Hawker 1988, Newman and Unger 2003).

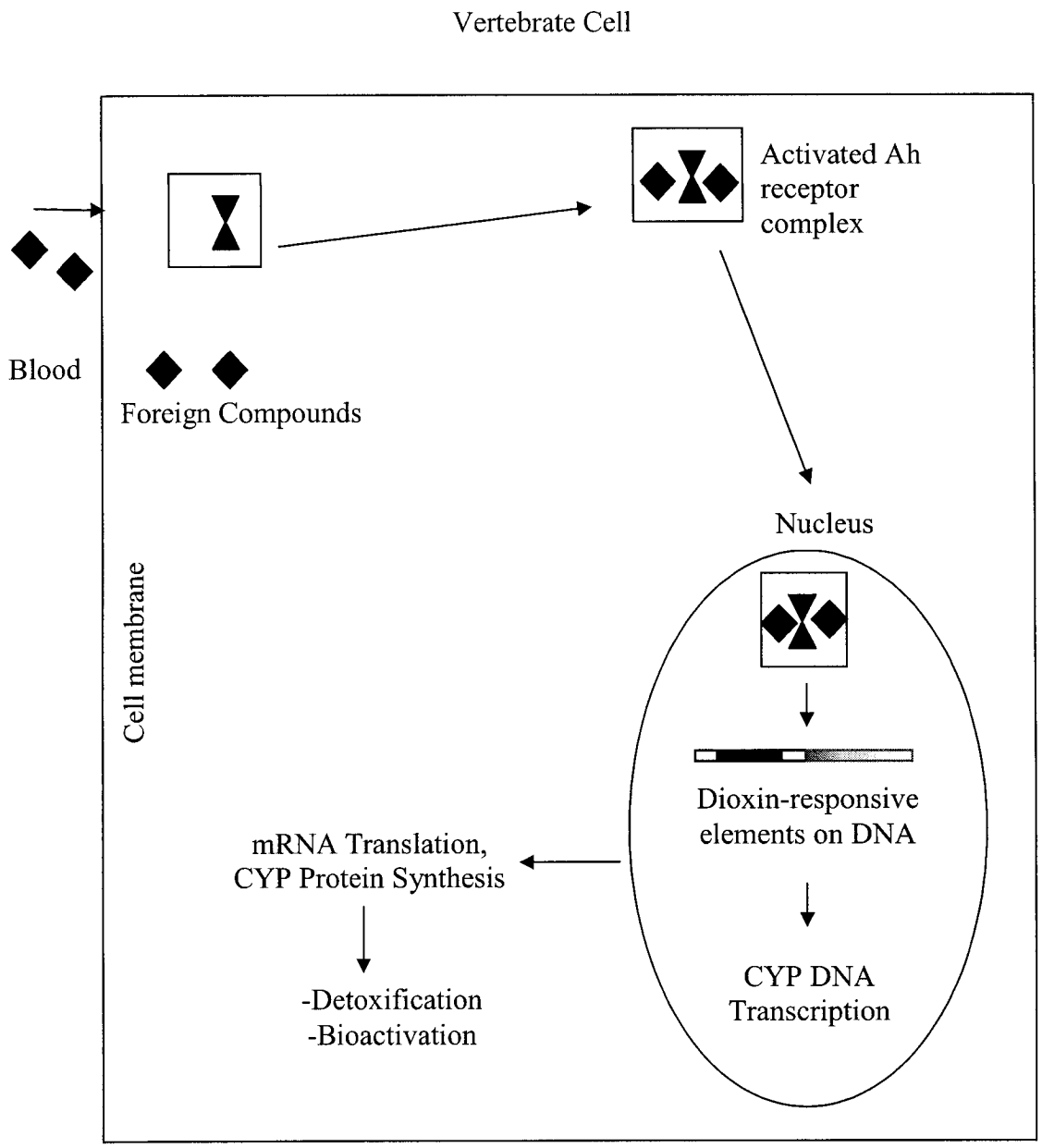


Figure 1.4 The mechanism of mixed function oxidase (MFO) induction.

Foreign substances enter the cell and bind to the Ah receptor, forming an activated Ah receptor complex that complexes with an Ah-receptor nuclear translator protein and enters the nucleus, where it interacts with the dioxin-responsive elements on DNA, enabling gene transcription to CYP mRNA, and translation, resulting in CYP1A1 protein formation. (Feeley and Grant 1993, Hodson et al. 1998).

2.0 Methods

2.1 Study Site

The magnesium smelter Magnola Metallurgy Incorporated is located in the Eastern Townships of Quebec in Danville, which is approximately 45°45'30".3 North and 72°00'21".7 W at an elevation of 190m. Located in the Great Lakes – St. Lawrence forest region, this upland area is characterized by rolling terrain and deep stream-cut valleys with mixed forests, comprised of sugar maple, basswood and white elm, eastern white cedar, beech and largetooth aspen (Rowe, 1972). Soils in the regions are typically well drained loam and Podzols with a thick till (Vassuer, 2000). The prevailing wind direction in the region was toward the north-east coming from approximately 245° in the southwest during the time the smelter was operational from 2000 to 2002 (Figure 2.1, and Appendix 2.1- 2.4) (Environment Canada 2005).

2.2 Sampling

Sampling began in 1999 prior to the smelter's opening in 2000, and continued while the smelter was operational in the years 2000, 2001, and 2002. Each sampling took place on the last weekend in October and first weekend in November, which is when deer hunting is permitted by Quebec's Societé de la Faune et des Parcs. Samplers were stationed outside of the one official deer registration office in the region and permission for sampling was solicited by the hunters. The locations of the deer kills were identified by each hunter, marked on a map, and later digitally recorded using Geographic Information Systems ArcView 3.2 mapping software (Figure 2.2).

At the hunting registration location in Danville, adipose tissue of freshly hunted deer was cut from inside the hind leg of the deer with dissection instruments, and tissue was wrapped in the pre-cleaned tin foil and placed in a marked ziplock bag. All instruments and

tin foil were sterilized prior to use by washing in industrial grade detergent and rinsing 3x with deionized water, then 3x each with ACS grade acetone and hexane, and stored in a glassware oven at 200°C for 12 hours. A total of 90 fat samples were collected in 2002, and of these, 43 were selected for PCB and OC analysis. In 1999, 123 deer were sampled and 33 were selected for PCB and OC analysis. Twelve of the 2002 fat samples were selected for PCDD/F analysis (Figure 2.3). Liver samples (n=14) (Figure 2.3) were wrapped in sterile foil, stored at -80°C in ziplock bags until returning to the University of Ottawa where they were stored in a –80°C freezer until analysis.

For extraction of the teeth, both incisors were removed by weakening the ligaments holding the tooth to the jaw bone by repeatedly wedging a scalpel between the tooth and the gum about 2cm below the gum line (Nelson, 2001). When the tooth was sufficiently loose, it was extracted using tweezers with its roots intact and wrapped in sterile foil. The tissues of each deer were placed in separately labeled plastic ziplock bags and stored on-site in a –20°C cooler until they were returned to the University of Ottawa where they were stored in a –20°C freezer until extraction. Deer ageing was done using a standardized cementum aging technique on the front incisors, which involved counting the cementum growth annular ring pattern on the tooth (Matson 1985, Delver 2000).

2.3 Polychlorinated Biphenyls and Organochlorine Pesticides

2.3.1. Chemicals

All of the solvents used, namely acetone, hexane and dichloromethane, were Omnisolv® high-purity grade from VWR (Mississauga, Ontario, Canada). All extracts were evaporated in iso-octane (Fisher Scientific, Fairlawn, NJ, USA). Anhydrous granular sodium sulfate (ACS Grade, EMD Chemicals, Gibbston, NJ, USA) and 100% activated silica gel (Davisil 635 Type 60A, Fisher Scientific, Fairlawn, NJ, USA) were muffled at 600°C for 6

hours and stored in an oven at 130°C for de-activation. Glass wool (VWR Scientific, West Chester, PA, USA) was sonicated in DCM and dried under N_2 and finally stored in a chemical oven at 130°C. Petroleum ether rinsed Hydromatrix (P.E. Hydromatrix, Varian Inc., Mississauga, ON) was used for lipid determination.

The field and lab surrogates and standards were as follows: PCB 30 and 204 surrogate standards (PCB 30 @ 110 pg/ul, PCB 204 @ 101.9 pg/ul), CB/OC field (1,3,5,TBB@ 103 pg/ul, 1,2,4,5 TTBB @ 100 pg/ul, delta-HCH@ 101 pg/ul), and CB/OC lab surrogates (1.3. DBB @ 103g/ul and Endrin Ketone @ 102pg/ul) and were obtained from the National Laboratory for Environmental Testing (NLET) in Burlington, Ontario, Canada. The internal standard Mirex (@ 105.96 pg/ul) was obtained from Ultra Scientific (North Kingstown, RI, USA).

2.3.2 Extraction

The extraction followed methods from The National Wildlife Research Centre in Ottawa (Won et al. 2001). 0.5g of fat was cut from the sample using a scalpel and ground with 25g of treated anhydrous Na_2SO_4 in a mortar and pestle until the mixture was uniform in color and texture. The ground sample mixture was poured into a glass column (2.1cm ID, 2.5cm OD and 35cm length) with an attached 250ml glass reservoir, with treated glass wool wet-packed in hexane, and an additional 0.5 cm Na_2SO_4 was added to the column. Dissection instruments were rinsed 3x in a 1:1 (v/v) mixture of dichloromethane/hexane, and rinses were eluted until solvents were level with the top of the tissue mixture. All PCB and OC field and lab surrogate standards were added to each column with 2-3 rinses in DCM/hexane (1:1 v/v) performed after the addition of each surrogate. After each column was soaked for 30 minutes, 200ml DCM/hexane (1:1 v/v) was eluted and the sample was collected in 2 fractions. These were evaporated on the Turbovap at 35°C with N_2 pressure at 1.2Barr or

18Pa and topped up with DCM and hexane to make up a final 8ml volume composed of equal parts DCM/hexane (v/v) for separation by gel permeation chromatography.

Lipid Determination was done using the accelerated solvent extractor (ASE, Dionex), an automated extraction technique that uses solvents at elevated temperatures and pressures. 0.5g of each sample was cut and ground in Hydromatrix and loaded into 33ml ASE cells. The cells were heated to 125°C at a pressure of 2000psi, flushed with DCM, and the lipid fraction was collected into a vial. The extract was evaporated to complete dryness and lipid content was determined gravimetrically using the formula:

Lipid content % = [(initial vial weight – final vial weight)/(tissue weight)]*100.

Sample clean-up was done by Gel Permeation Chromatography (GPC Autoprep 1002A, Analytical Bio-Chemistry Laboratories, Columbia, Missouri, USA). Samples (equal parts DCM/Hexane v/v) were injected onto a column packed with silica bio-beads and were evaporated down to <1ml on the turbovap. The organochlorine compounds were fractionated using silica acid gel columns. 8g of silica was wet-packed and rinsed with hexane. Each column was rinsed with 20mls of hexane, and then the 1ml sample was injected, followed by 3 hexane rinses. Each column was then eluted with 50mls of hexane and collected for fraction A (for extraction of non-polar compounds PCBs, aldrin, HCB, heptachlor, p,p'DDE), and then eluted with 80ml of DCM/Hexane (1:1 v/v) for fraction B (for extraction of more-polar compounds such as heptachlor epoxide, HCH's, chlordanes, dieldrin). Both Fractions A and B were evaporated down to 500 µl on the turbovap at 55°C and at 35°C, respectively, and transferred to 2ml amber glass GC vials (Kimble Glass Inc, Vineland NJ, USA) with 25 µl of internal standard Mirex was added to each and were stored in at 4°C until analysis.

2.3.3 Analysis

The 500 µl samples were analyzed by Hewlett Packard 6890 Series II gas chromatograph with a ^{63}Ni electron-capture detector, using splitless injection with an inlet temperature of 250°C and separated on a 30m x 0.25mm (0.25um film) DB-5MS column (J&W Scientific) using helium carrier gas at 3.1ml/min.

125 PCB congeners and 25 OC pesticides were separated out as chromatographic peaks and concentrations were determined with HP Chemstation software (Rev. A.06.03, Hewlett Packard, Paolo Alto, CA, USA). In the chromatograms certain congeners were coeluted in groups of two or three resulting in a total of 101 peaks. The concentrations of the coeluted peaks were expressed as one value, and the concentration of the coeluted congeners were multiplied by factors representative of their weighted distribution in the chromatographic peaks (Appendix 2.5). PCB concentrations were expressed as homologues comprising the following PCB congeners: monochlorinated (1,3), dichlorinated (4+10, 7+9, 6, 8+5, 12+13, 15+17), trichlorinated (18, 19, 15+17, 24+27, 16+32, 29, 26, 25, 31+28, 22, 33+20), tetrachlorinated (54, 31+28, 53, 51, 45, 52, 49, 43, 48+47, 44, 59+42, 40, 63, 74, 70+76, 66, 55, 56+60, 81), pentachlorinated (98, 91, 100, 92, 84, 101, 99, 119, 83, 97, 87, 85, 110, 82, 107, 118, 114, 105), hexachlorinated (136, 151, 135+144, 147, 149, 133, 134+131, 146, 153+132, 141, 137, 130, 138+163, 158, 129, 128, 167, 156, 157), heptachlorinated (179, 176, 178, 175, 187+182, 183, 185, 174, 177, 171, 173, 172, 180, 193, 191, 170+190), octachlorinated (202, 200, 197, 199, 198, 201, 203+196, 195, 194, 205), nonachlorinated (208, 207, 206) and decachlorinated (PCB-209). Data analysis was performed using SYSTAT, version 10 (©SPSS Inc. 2000, Standard Version, Chicago, IL, USA).

2.3.4 Quality Control

The sample extraction method used in this study (Won et al. 2001) was validated in an interlaboratory performance test for PCB and OC analysis of mammal tissue by the National Institute of Standards and Technology (NIST). Six samples of whale blubber control material (Marine Mammal Quality Assurance Exercise Homogenate VI and Standard Reference Material (SRM) 1945 Organics in Whale Blubber) were analyzed. Accuracy was evaluated with a z-score, which represented a ratio of the difference between the laboratory result and the exercise assigned value and the target value for standard deviation (25%). Precision was assessed with a p-score, which represented a ratio of the variance estimates (or coefficients of variance) for the lab and that of the target variance (15%). Performance was considered satisfactory with z- and p- scores where absolute value is ≤ 2, and all of the PCB congeners were within this limit, as well as OCs HCB, Dieldrin, and a-HCH (Appendix 2.6) (Kucklick et al. 2004). These results ranked the present lab among the best out of 24 international laboratories participating in this official round-robin testing.

Consistency of the column extraction method used from The National Wildlife Research Centre (Won et al. 2001) was verified by taking eight replicates from one sample (# 573) and the standard error was 1.1ng/g, approximately 3.14% of the mean (36ng/g). This particular sample was also analyzed using the accelerated solvent extractor (ASE) (n=1), and the resulting PCB concentration was within 1 standard deviation of the mean PCB concentration from the column extractions (n=8) (Appendix 2.7).

Average surrogate recoveries and standards errors of PCB 30 and PCB 204 were 55% ±1.8% and 62% ± 1.9% taken from a total of 101 samples, including method blanks (n=18) and samples (n=83). For organochlorine pesticide surrogates the recoveries and standard errors were 45%±1.5% for 1,3 DBB, 45%±1.2% for 1,3,5 TBB, 45%±1.5% for

1,2,4,5 TTBB, 48% ±1.6% for d-HCH and 66%±2.8% for Endrin Ketone. Due to the variability of recoveries between sample sets, corrections were made for surrogate recovery efficiencies.

One method blank was run with every set of five samples. Each sample was blank corrected on a congener-by-congener basis using the bank within its particular set. Method detection limits were calculated as an average of the method blanks (n=18) ± 2*SD (Gouin et al. 2004) and the detection limits were reported as 2*SD because the blanks were subtracted at the onset of the analysis. The detection limit for ∑PCB was approximately 1759pg/g and ranged from <0.1 to 632.34 pg/g for individual congeners (Appendix 2.8). For hexachlorobenzene the detection limit was approximately 769pg/g and other organochlorine pesticides ranged from <0.1 to 476 pg/g (Appendix 2.9).

2.4 Dioxins and Furans and Coplanar PCBs

2.4.1 Method of Analysis

The analytical procedure that was used for PCDD/Fs and coplanar PCBs is described in the Laboratory Services Methods Manual by Simon and Wakeford (2005) and is CAEAL (Canadian Association for Environmental Analytical Laboratories) accredited. Briefly, the column extraction and gel permeation chromatography clean-up followed the same protocol as used for the PCBs (2.3). This was followed by an alumina (basic, Brockman activity 1, 60-325 mesh, Fisher Scientific, A941-500) column clean-up. The separation of PCDDs, PCDFs, and co-planar PCBs from other OC compounds was achieved using an automated carbon/fiber column chromatograph (Chromat-A-Trol Model II (Eldex) controller, Eldex Model E-120-S pump). After desorption with toluene (Omnisolv, BDH TX0737-1), coplanar PCBs were separated from PCDD/Fs using florisil (pestidice grade, 60-100 mesh, BSH B28722-38) column chromatography.

Quantitative analysis of PCDDs, PCDFs and coplanar PCBs was performed with a VG AutoSpec double-focusing high-resolution mass spectrometer fitted with an HP 5890 Series II high-resolution gas chromatograph. An Alpha VMS data system provided data collection and instrument control. Chromatographic interpretation was performed using software Mass Lynx V4.0.

2.4.2 Quality Control

Two method blanks and three quality control samples (herring gull egg homogenate prepared in-house) were analyzed in addition to the fat samples. The analytical samples were spiked with standard solutions, and the coplanar PCB and PCDD/F batch calibration standards were prepared using the solutions specified in appendix 2.10.

The internal standard recoveries were deemed acceptable according to EPA Method 1613 standards. Recoveries were within normal parameters for this method, and averaged 82% ±1% standard error for PCDD/Fs, and 61%±2.2% for coplanar PCBs. Recoveries and concentrations (wet weight) for PCDD/Fs were calculated manually based on RRFs (relative response factor) for the calibration standards due to inconsistencies in the calibration curve calculations generated from Mass Lynx V4.0. Manual calculation was also performed for additional projects that had been performed at NWRC since September 2004 and was not specific to this sample batch. Additional quality control laboratory testing on two egg batches at NWRC (A48 and A37) and on two sets of standards ("old"- use prior to September 2004, and "new" –use after September 2004; PCDD/F ^{13}C Spiking solution #22B and #22C) verified that inconsistencies were not due to standard concentrations or irregularities in the egg batches.

The limit of detection (LOD) was set at 3:1 signal to noise and the limit of quantification (LOQ) was set at 10:1 signal to noise. These values were calculated for each compound and sample (Appendix 2.11).

2.5 Hepatic Mixed Function Oxidase Induction

The expression of hepatic cytochrome P4501A1 enzymes in deer liver (n=14) was measured in an ethoxyresorufin-O-deethylase (EROD) bioassay, where EROD catalyzed a reaction, initiated by NADPH, resulting in the formation of resorufin from 7-ethoxyresorufin (Kennedy and Jones 1997). This was performed using a standard method from Kennedy and Jones (1994, 1997) and a brief summary is provided in this section.

2.5.1 Equipment

The fluorescence mutiwell plate reader was a SpectraMax Gemini XS from Molecular Devices (Sunnyvale, CA, USA) equipped with a Xenon flash lamp (1 joule/flash) and a R-3896 photomultiplier. It was controlled using an A0Open Pentium II computer. A Spectramaxplus 384 spectrophotometer from Molecular Devices (Sunnyvale, CA, USA) was used for protein assays. EROD assays were carried out in Falcon 48-well plates placed on a dry block heater (VWR Scientific).

2.5.2 Reagents

Fluorescamine (M.W. 278.3), BSA, Nicotinamide dinucleotide phosphate NADPH (M.W. 833.4), Resorufin (M.W. 235.2), 7-ethoxyresorufin (M.W. 241.2) were obtained from Sigma Chemical Co. (Toronto, Ontario). Sodium phosphate dibasic (M.W. 141.96) and monobasic (M.W. 137.99), methanol (MeOH) (HPLC grade) and Acetonitrile (HPLC grade), Glycerol (20% v/v), EDTA (368.4g/mol), and ß- mercapoethanol (78.13g/mol) were purchased from Fisher Scientific Co (Ottawa, Ontario).

2.5.3 Resorufin and Protein Standard Curves

Resorufin produced by EROD was derived from a resorufin standard curve, and total proteins determined from the BSA standard curve were used to determine the EROD activity (pmol RESORUFINmin^{-1}mg^{-1} proteins). A total of 4 plates (hence 4 sets of standard BSA and resorufin curves and sets of calculations) were used (Appendix 2.12). These calculations were performed according to method MET-BMK-EROD-01E (Kennedy and Jones 1997). Standards were prepared on 18 of the wells on the 48-well plate used for the EROD assays, with 15 of these wells containing different volumes of both BSA and resorufin, and 3 wells with neither of the standards. Reagents were added in appropriate quantities using the array shown in Table 2.1: Sodium phosphate buffer (0.05M, pH 8) was added to all 18 wells with volumes ranging from 47-135ul; BSA (1.96mg/ml prepared in phosphate buffer) was added to 15 of the wells at volumes ranging from 10-80ul (yielding final concentrations ranging from 58.5 to 468 ug/ml); and the remaining reagents were then added in the following order: resorufin (stock solution 152uM in MeOH, working solution 15uM diluted in buffer) with volumes ranging from 1-8ul (yielding final concentrations ranging from 44.77 to 358.2nM), 50ul of ethoxyresorufin in each well (stock solution 1165uM in MeOH, working solution prepared immediately prior to addition 9.4uM diluted in buffer) yielding a final concentration of 1.4uM, 50ul NADPH (2.4mM diluted in buffer, final concentration 0.36mM), and 100ul of fluorescamine (2.16mM in acetonitrile, final concentration 0.64mM).

2.5.4 Microsome Preparation

All liver samples were maintained at 4°C on ice for the duration of the microsome preparation. The samples were thawed on ice for 10 minutes, and 0.6g of each was cut using a scalpel and scissors, and homogenized in a glass tube with 10 up and down strokes using a

homogenizer with a Teflon pestle in 600ul of sodium phosphate buffer (0.05M). Samples were then transferred to Eppendorf microcentrifuge tubes and centrifuged for 20 minutes at 4°C at 10,000g or 11,000rpm on a Beckman Coulter Microcentrifuge R Centrifuge. The supernatant was transferred to an Eppendorf microcentrifuge tube for high speed centrifugation for 1 hour at 4°C at 49,000rpm. The excess liquid was drained, and the resulting pellet was rinsed with 200ul of sodium phosphate buffer (0.05M). The pellet was broken down and resuspended with 600ul of resuspension buffer, which was comprised of EDTA (1mM), glycerol (20% v/v) and β-mercapoethanol (1mM, 78.13g/mol). For each sample, 3 aliquots of 200ul each were frozen at -80°C.

2.5.5 Ethoxyresorufin-O-deethylase assay

Using the array shown in Appendix 2.12, 24 of the wells on the 48-well plate were used for 6 samples, each in triplicate with one blank. Sodium phosphate buffer (0.05M, pH 8) was added to all 24 wells, and each well then received a 20ul volume of microsomes. 50ul of ethoxyresorufin (stock solution 1165uM in MeOH, working solution prepared immediately prior to addition: 9.4uM diluted in buffer yielding a final concentration of 1.4uM) was added to each well and the plate was pre-incubated on a dry block heater for 5 minutes at 37°C. The reaction was initiated by the addition of 50ul of NADPH prepared immediately prior to use (2.4mM diluted in buffer, final concentration 0.36mM) to all wells except the blanks. Plates were incubated for 10 minutes at 37°C on the dry block heater after which the reaction was halted by the addition of 10ul of fluorescamine (2.16mM in acetonitrile, final concentration 0.64mM). The plate was then left at room temperature for 15 minutes to allow for stable fluorescence and scanned on the fluorescence plate reader with a 530-nm excitation filter (25-nm bandwidth) and a 590-nm emission filter for resorufin, and

using a 400-nm excitation filter (35-nm bandwidth) and a 460-nm emission filter to obtain fluorescamine protein measurements. Fluoresence data was imported into Quattro Pro version 9.0 for Windows (Borland) for curve fitting.

2.6 Statistical Analysis

For PCBs and OCs, a 1-way ANOVA was used to indicate significant differences in PCB concentrations between data from 1999, a year before the smelter opened, and 2002 deer. A Before-After Control-Impact ("BACI") design was used to compare 1999 and 2002 deer which were near (<5km) and far (>15km) from the smelter. This analysis was based on a 2-way ANOVA with the distance and year groups as factors. For detection of an effect, each factor and the interaction term had to be significant (E.P. Smith 2002). In an additional test, PCB concentrations were regressed against distance using both 1999 and 2002 individuals. An ANCOVA model tested the homogeneity of the slopes between the two linear regressions. Significance was reported only if the 2002 regression was significant, and if the slopes were significantly different between 1999 and 2002 (ANCOVA). Random numbers between 0 and the detection limit were generated using a microsoft excel 2002 (SP3) function for PCB values that were below the instrument detection limit (zero values) in order to normalize the data. This procedure reduces statistical bias because it better approximates the total variance in the samples (Stern et al. 1997, Davidson 2002). This was necessary for the homologue groups monochlorobiphenyl, dichlorobiphenyl, octachlorobiphenyl, nonachlorobiphenyl and decachlorobiphenyl and for all of the PCB congeners because some of the samples were below detection limit (Appendix 3.3).

Distance regressions were run with PCDD/F concentrations and EROD induction. All concentration data were $\log_{10}$ transformed for normality. Overall, assumptions were tested and met for the linear regressions, ANOVAs and ANCOVA models. Normality was tested

using a 1-sample Kolmogorov-Smirnov (Lilliefors) test on the residuals, by visual inspection of a normality probability plot of residuals, and by examination of the ratio of skewness / standard error of skewness and kurtosis / standard error of kurtosis (S/SES and S/SEK<|2|). Independence was verified by the Durbin-Watson D- statistic (2±0.5) and by an autocorrelation plot (<|0.5|). Homoscedasticity was validated using Levene's test, and visually by a plot of studentized residuals (Zar 1999, Morin and Findlay, 2002). All analyses and calculations were conducted by SYSTAT Version 10 Statistical Software.

In the human health risk assessment, the intake of each contaminant in a single meal portion was calculated using the equation below (Health Canada 1994).

Dose (pg TEQ.kg^{-1}.week^{-1}) = C_{Food} x IR_{Food} / BW

Where:

C_{Food} = concentration of contaminant in food (pgTEQ.g^{-1})

IR_{Food} = receptor ingestion rate for food (g/week)

BW = body weight (kg)

Standardized body weights and portion sizes were used in the calculation (Health Canada 1994, Easton et al. 2002, Hites et al. 2004). A lipid correction was applied to the calculation because the contaminant levels in this study were measured in deer fat, whereas people consume the venison muscle which has a very low fat content (1.87%). This value was determined by laboratory measurement of in actual deer muscle samples, and from lipid content of deer reported in a similar study (Gabos et al.1998).

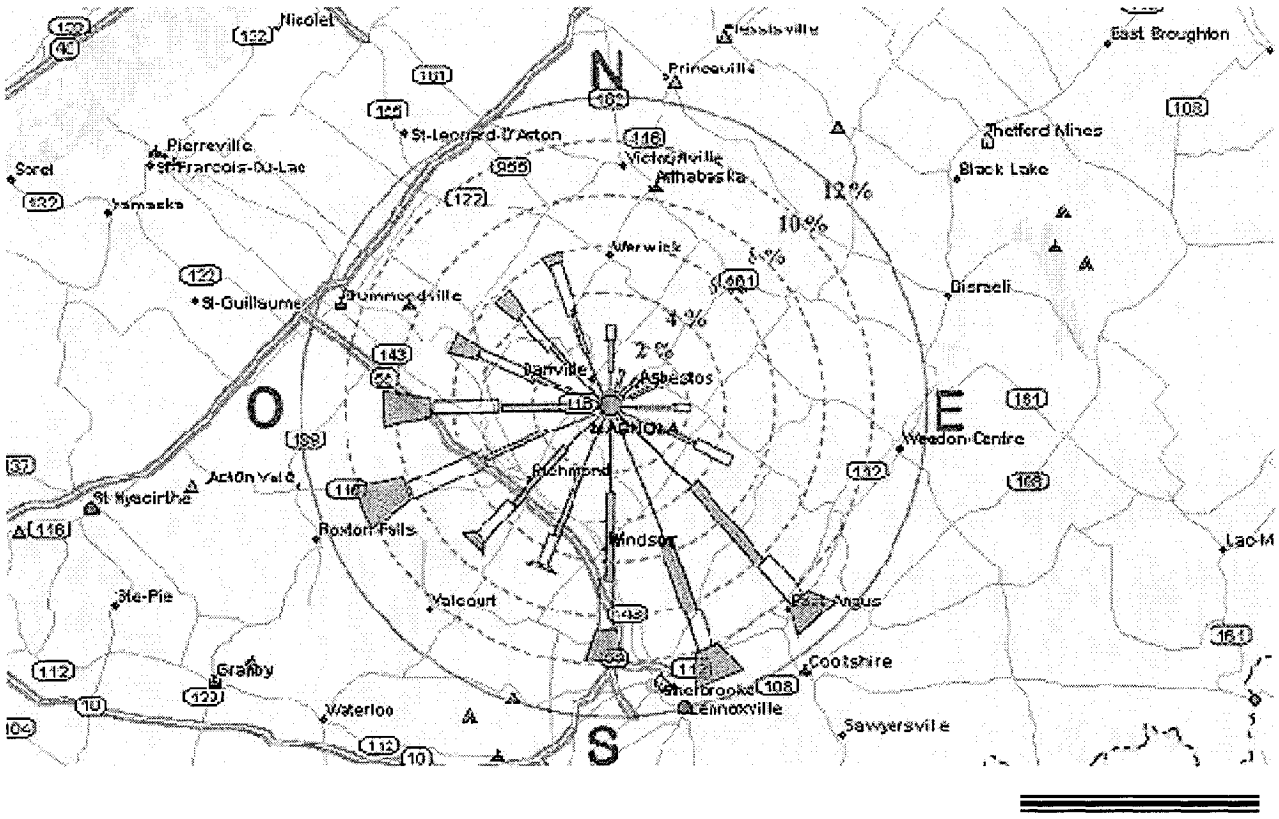


Figure 2.1 The prevailing wind direction in Danville, Quebec.

The smelter is shown in the centre of the map. The bars represent wind vectors pointing in the direction the wind is coming from and their size is weighted according to the wind speed (Hatch and Associates 1997).

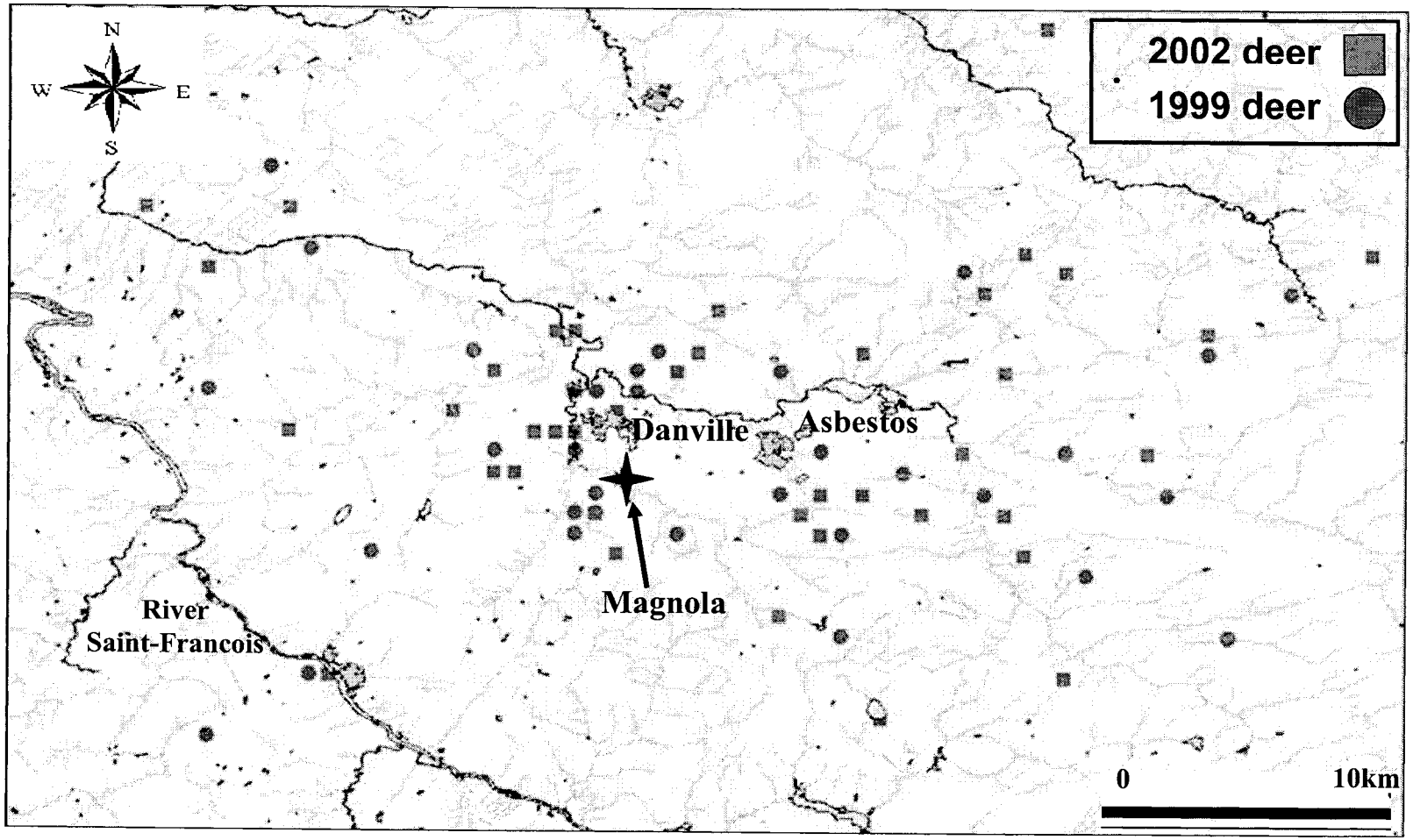


Figure 2.2 Sampling Sites in Danville, Quebec.

Deer samples in 1999 (n=33) and 2002 (n=43) are shown in proximity to the smelter, indicated in the centre of the map.

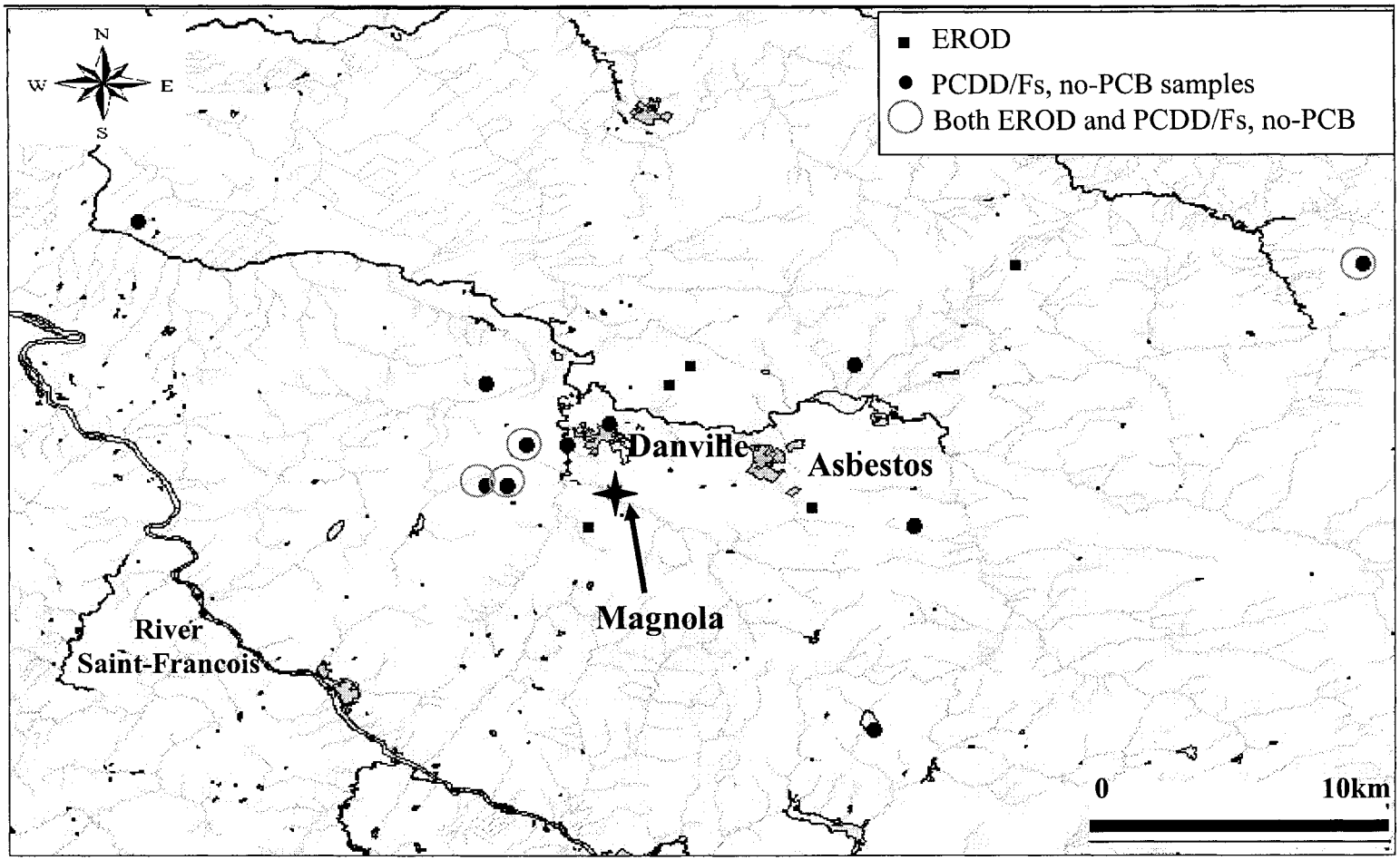


Figure 2.3 Sampling sites of 2002 deer analyzed for PCDD/Fs, coplanar PCBs, and EROD in Danville, Quebec.

2002 deer samples are shown in proximity to the smelter, indicated in the centre of the map.

3.0 Results

3.1 Polychlorinated Biphenyls and Hexachlorobenzene

The mean total PCB concentrations in 2002 were 1.5 times greater than in 1999 (Table 3.1). Means for total PCBs and for the homologues hexachlorobiphenyl, octachlorobiphenyl, nonachlorobiphenyl and decachlorobiphenyl and PCB congeners 16-32, 31-28, 52, 66, 99, 101, 133, 136, 153-132-105, 158, 138-163, 187-182, 202-171-156, 191, 193, 201, 206, 207 and 209 were significantly elevated in the 2002 deer samples (n=43) relative to the control samples (n=33) from 1999 ($P<0.05$) (Figure 3.1, 3.2). On average hexachlorobiphenyls were present in the greatest abundance (31.7%) relative to other congener groups in the 2002 samples followed by penta- (18.7%) and hepta- (16.7%) chlorobiphenyl while tetra-, di-, tri-, octa-, nona- and deca- chlorobiphenyls were minor constituents in deer (Table 3.2 and Appendix 3.1).

There was a difference in abundance between the PCBs in deer that were near the site (<5km, n=10) and at far range (>15km, n=15) in 2002 (Figure 3.3). These particular distance groupings were selected because the deer in the Danville region are considered non-migratory due to an abundance of food in the area (M. Crete, Société de la Faune et Parcs du Quebec and Département de Biologie Université Laval, personal communication), and based on home range sizes reported in Quebec, North American, and European white-tailed deer (0.67-24km^2; 24 km^2 being unusually large compared to 6 other studies which report ranges below 3.19 km^2), which are well within the area designated as "near" to the smelter (<5km), encompassing approximately 78.5km^2 (Table 1.5). Additionally various studies finding evidence of local contamination in soil and vegetation have done so within 5km of a point-source (Bright et al. 1995a, Kuzyuk 2000, Blais et al. 2003, Pier et al. 2003). Although 20km is a commonly used boundary for far-range sites, 15km was chosen in this study because of a

greater sample size in this group, and differences in PCB concentrations between the 15km and 20km groupings were insignificant in the deer samples.

$\sum$PCB concentrations in the deer close to the smelter (<5km, n=10) were consistently higher than those further away (>15km, n=15) in 2002 deer, with concentrations and standard errors of 10 ±2.9ng/g and 5.9 ±0.8ng/g, respectively. In a BACI design, a 2-way ANOVA showed that log concentrations of $\sum$PCBs, hexa-chlorobiphenyls, and octa-chlorobiphenyls were significantly different ($p<0.05$) between the 1999 and 2002, and that there were significant differences between the near (<5km) and far (>15km) groupings in 2002, but not in 1999 (Figure 3.3). In 2002, the mid-range PCB homologues, namely hexachlorobiphenyl, heptachlorobiphenyl and octachlorobiphenyl, were present in greater proportions near the smelter compared to deer that were far (Table 3.2, Figure 3.4). Mid-range PCB congeners showed this trend, for example PCB 138-163 (near 9.87±4.45% versus far 6.54±1.16%) (Table 3.2). In general, lower-chlorinated congeners did not an effect of distance from the smelter. For example, as PCB 31-28 was not in greater abundance in near compared to far individuals (near 2.65±0.54% versus far 4.05±0.85%) (Table 3.2, Appendix 3.1).

Total PCB concentrations in the 2002 deer showed a significant inverse relationship with distance ($r^2= 0.21$ $p<0.01$) and an ANCOVA model showed that slopes of the 1999 and 2002 regression lines were significantly different ($p<0.01$) (Figure 3.5). Similarly, significant differences between 1999 and 2002 slopes and a significant decline in concentrations with distance in 2002 was observed for the homologue groups pentachlorobiphenyl, hexachlorobiphenyl, heptachlorobiphenyl and octachlorobiphenyl (Figure 3.6) and this was mirrored in select congeners from these groups, particularly PCBs 99,101, 138-163, 187-182, 193 and 201 (Figure 3.7a, Table 3.3, Appendix 3.2). PCBs 153-

132-105, 133, and 177 showed significant declines with distance in 2002, and the difference in slopes between 1999 and 2002 was close to significance ($p<0.1$) (Figure 3.7b). Similarly, the negative linear relationship between the concentrations of PCB -118 and -180 and distance in 2002 was close to significance ($P<0.1$) (Figure 3.7b). The mono, di, tri, tetra, nona and deca- chlorobiphenyls did not show a decreasing relationship with distance in the 2002 deer and the slopes between the 1999 and 2002 deer were not significantly different. These homologues were mostly non-detect, with 86%, 58%, 54%, 44%, and 48% of the samples below detection limits, respectively (Appendix 3.3). PCBs 31-28, 52 and 74 and 209 were selected to represent these homologues and displayed no decline with distance (Table 3.3).

Age of the deer did not have a significant effect on PCB concentrations. Although there were significant differences in PCB concentrations between the 1999 and 2002 deer, no differences were found between juveniles and adults (age groups 0-1and ≥2years), nor between deer feeding during the time the smelter was open (0-2years) and those that were alive prior to the smelter's activities (>2 years).

Hexachlorobenzene

Hexachlorobenzene (HCB) was a known emission product from the smelter and concentrations were above the detection limits whereas other organochlorine pesticides that were non-emission products, such as Aldrin, Heptachlor, Endrin, β-endosulfan, pp-DDT, and pp-DDT were mostly non-detect and showed no trends over space and time (Appendix 3.4). There were significant differences between the 1999 and 2002 concentrations of HCB ($p<0.05$) and this was not found for non-emission products, for example, α-endosulfan (Figure 3.8). The differences were not related to distance, age or prevailing wind direction.

Out of 24 organochlorine pesticides analyzed, concentrations of dieldrin, declined with distance in 2002 ($p<0.05$) while it did not in 1999 and there were significant differences between the years.

3.2 Dioxins and Furans and Coplanar PCBs

The relative abundance (%) of PCDD/Fs in pg/g concentrations in the deer showed that OCDD/Fs were present in the largest proportions (13-16%). The penta-, hexa- and hepta- CDD/Fs were between 3-6%, and the tetra PCDD/Fs were present in the smallest proportions (Figure 3.9c). With the relative abundances (%) expressed as pgTEQ/g concentrations (Figure 3.9b), the Penta-CDD/Fs were present in the greatest proportions mainly due to their high TEFs, which are 0.5 for 2,3,4,7,8-PeCDF and 1.0 for 1,2,3,7,8-PeCDD. The TEQ concentration of 2,3,7,8- TCDD with a TEF of 1 was also present in greater proportions relative to its abundance profile expressed in pg/g concentrations, while the Hexa-CDD/Fs (TEF 0.1) remained in high proportions in both the TEQ (3-5%) and wet (4-6%) weight concentrations. OCDD and OCDF proportions expressed in pgTEQ/g were diminished compared to their profile expressed in pg/g, mainly due to their low TEFs of 0.0001 (Figure 3.9b). PCB-126 dominated the profile among the coplanar PCBs, accounting for approximately 62% of the total (pg/g) concentration, and PCB-169 and PCB-77 were present in lower proportions at 17% and 20% respectively. When the fractions (%) were expressed according to TEQ concentrations, PCB-126 accounted for 97% of the total toxic equivalency (pgTEQ/g), PCB169 for 2.7%, and PCB-77 for 0.3% (Figure 3.10).

Comparing the profiles of the stack emissions (Figure 3.9a) and the deer (Figure 3.10b), few of the PCDD/F congeners were present in similar proportions, namely 2,3,4,7,8-PeCDF with relative abundances of 20% and 22% respectively; 2,3,7,8-TCDD, with 3.5% and 6.6% respectively, and 2,3,4,6,7,8-HxCDF with 2.8% and 4.8%, respectively. The

Hepta-CDD/Fs and OCDD/Fs were consistently present in low proportions (0-2.5%) in both profiles. Bioconcentration factors (BCFs) were used to account for differences between the homologue profile in the stack emissions and the deer. BCFs represent the extent to which compounds concentrate in animal tissue from the contaminant levels in their diet, and these values were adopted from a model predicting PCDD/F transfer from air to cattle by Lorber et al. (1994) (Table 3.4). The ratio of the relative abundance of the PCDD/F congeners in deer from this study relative to air (stack emissions) showed a positive significant linear relationship with the BCF dataset (r^2=0.36, p=0.011), while the congener abundance in air did not (Table 3.4, Figure 3.11). This indicates that the high BCF values coincided with the homologues which concentrated to a great extent in the deer in this study, while the low BCF values coincided with the homologues that were present in high abundances in the stack emissions but did not concentrate in the deer to a great extent.

The concentrations of PCDD/Fs and coplanar PCBs are greater in those samples in close range to the smelter compared to those at greater distances (Appendix 3.5, 3.6). There is a contrast between the TEQ concentrations (pgTEQ/g) in the samples within 5km (n=6) and those between 5 and 20km (n=4), with mean $\sum$ PCDD/F (±SE) concentrations of 7.26±4 pg TEQ/g and 4.62±2.21 pg TEQ/g (Figure 3.12), and mean $\sum$no-PCB (±SE) concentrations of 3.93±1.72 pg TEQ/g and 0.63±0.69pg TEQ/g (Figure 3.13b), respectively. An even greater contrast is present when comparing the latter groups with samples beyond 20km (n=2), which showed a comparatively low mean $\sum$ PCDD/F concentration of 0.64±0.28 pg TEQ/g (Figure 3.12), and a mean $\sum$no-PCBs (±SE) concentration of 0.51 ±0.13 pg TEQ/g (Figure 3.13b). A similar decline in coplanar PCB and PCDD/F wet weight concentrations (pg/g) with distance from the smelter was seen in a contrast between the samples within 5km (n=6) and those between 5 and 20km (n=4), with mean $\sum$PCDD/F concentrations (±SE) of

55.8±31.9 pg /g and 30.5±18.1 pg/g (Figure 3.14), and mean ∑no-PCB concentrations (±SE) of 58.7±20.3pg/g and 13.8±1.72pg/g, respectively (Figure 3.13a). Samples beyond 20km (n=2) yield even lower contaminant levels, with mean ∑PCDD/F concentrations (±SE) of 5.92±1.58 pg/g (Figure 3.14), and mean ∑no-PCB concentrations (±SE) of 10.4 ±2.64 pg/g (Figure 3.13a). The variation present in the range of samples within 5km from the smelter may be due to the fact that they are from different spatial regions, and not all lie within the prevailing wind direction relative to the smelter.

Dioxins and furans in deer from 2002 were regressed against distance from the smelter using a greatly reduced sample size (n=12) than what was used for the PCB analysis (n=43). ∑PCDD/Fs did not show a significant decline with distance (r^2=0.095, p=0.16), and when expressed as TEQ concentrations, the relationship improved slightly (r^2=0.121, p=0.13) (Figure 3.15). The most toxic congener 2,3,7,8-TCDD with a TEF of 1 demonstrated the most significant decline with distance relative to the others (r^2=0.19, p=0.099). ∑HxCDD (r^2=0.106, p=0.15), 1,2,3,7,8-PeCDD (r^2=0.12, p=0.136) and OCDD (r^2=0.115, p=0.14) also showed more significant relationships relative to other congeners (Figure 3.15, Table 3.5). ∑no-PCBs showed a significant decline with distance (r^2=0.37, p=0.018), with PCB-126 being the most significant (r^2=0.4, p=0.014) followed by PCB-169 (r^2=0.3, p=0.033) and PCB- 77, which was close to significance (r^2=0.2, p=0.072) (Figure 3.16, Table 3.5).

3.3 Ethoxyresorufin-*O*-deethylase Activity (EROD)

In this study EROD activity measured in the liver showed a significant decline with distance from the smelter (p<0.05, r^2=0.46) (Figure 3.17). EROD activity and ∑PCB in deer fat showed a positive linear relationship that was close to significance for ∑PCB (r^2=0.2, p=0.053, n=14).

3.4 Risk Assessment

3.4.1 Human Health

The risk of adverse health effects posed to humans by contaminated feed was analyzed by applying PCB, HCB and dioxin and furan levels measured in the deer in this study to consumption guidelines. Health Canada's TDI's (tolerable daily intake) for HCBs is 270 ng kg^{-1} bw day^{-1} kg and that for PCBs has recently been lowered from 1000 ng kg^{-1} body weight per day^{-1} to 130 ng kg^{-1} bw day^{-1} (Health Canada 2001, Feeley, M., Health Canada, personal communication). These were applied to the deer fat samples and consumption of deer meat was unrestricted by the consumption guidelines.

The WHO (World Health Organization) specifies a consumption range for coplanar PCBs and PCDD/Fs of 1-4 pg TEQ kg^{-1} bw day^{-1} (WHO 2000). Health Canada guidelines stipulate a tolerable monthly intake (PTMI) of 70 pg kg^{-1} bw $month^{-1}$, which lies approximately in the middle of the WHO range at 2.5 pg TEQ kg^{-1} bw day^{-1}. The Health Canada guideline was provisionally adopted from a recommendation of the FAO/WHO Expert Committee on Food Additives (Health Canada 1994, JEFCA 2001, Feeley, Health Canada, personal communication). The PCDD/F samples were grouped into categories to best represent the different levels of risk associated with deer at varying distances from the smelter: the first sample represents a maximum value which was located within 5km of the smelter and in the prevailing wind direction (northeast); the second group consisted of samples within 5km of the smelter in all geographic directions (n=6); the third between 5 and 15km of the smelter (n=4); the fourth beyond 20km (n=2), and an average of all samples (n=12) was calculated. The number of portions required to exceed safe levels increased with the distance from the smelter (Table 3.6). According to the lower-bound limit of the WHO guidelines (1 pgTEQ kg^{-1} bw day^{-1}), more than three 227g portions per week of venison (12

per month) from the deer within 5km of the smelter and in the prevailing wind direction (maximum value) would exceed safe limits, in contrast to an unrestricted number of meals for the deer grouping beyond 20km of the smelter. The Health Canada guideline allows for no more than 30 meals per month (extrapolated to 7.5 per week) of deer within 5km of the smelter and in the prevailing wind direction, and an unrestricted number of meals in deer beyond 20km of the smelter.

For toddlers and children, the intake limits were more restrictive (Table 3.7). For toddlers (7 months – 4 years of age), the number of weekly portions that could be safely consumed according to the lower-bound limit of the WHO TDI should not exceed one and a half a portions of deer within 5km of the smelter and in the prevailing wind direction (maximum value), and 5 portions for deer that lay within 5km in all cardinal directions (N,S,E,W). With the same criteria applied for children (5-11 years), limits were slightly higher, at 2 portions per week for the maximum value deer, and 7 portions of deer within 5km and in all cardinal directions around the smelter. Health Canada's guideline limits intake to no more than 3.5 and 5 portions per week of the maximum value deer for toddlers and children, respectively, whereas the limits lie beyond realistic consumption for deer in other location groupings (Table 3.7).

Recently Health Canada surveyed regional dietary intakes of dioxin-like chemicals from foodstuffs in Canada and determined the PCDD/F TEQ concentrations of foodstuffs in Montreal (Health Canada 1993[1]). One deer located within 5km of the smelter and in the prevailing wind direction has the highest PCDD/F and coplanar PCB levels (0.725pf TEQ g^{-1}) compared to other foods (Table 3.8). Deer located within 5km of the smelter and in all cardinal directions (N,S,W,E) had a mean concentration of 0.209pg TEQ g^{-1}, ranking the 11th

highest contaminated food, and deer located beyond 20km ranked among foods with the lowest PCDD/F concentrations (Table 3.8).

3.4.2 Wildlife

In the most recent Arctic Monitoring and Assessment Programme (AMAP) report, the health risks that PCDD/Fs and coplanar PCBs pose to terrestrial mammals such as wild caribou and reindeer was evaluated by comparing their TEQ concentrations with threshold values for immunosuppression in harbour seals as determined by Ross et al. (1995) (de March et al. 1998, de Wit et al. 2002). In this study, ∑PCDD/Fs levels in the maximum value deer located in the within 5km of the smelter and in the prevailing wind direction (25.14 pg TEQ g^{-1} lipid weight) were above this threshold, and the other deer samples (n=11) were below it (0.35-8.07pg TEQ g^{-1} lipid weight). The thresholds defined for coplanar PCBs and the sum of PCDD/Fs + no-PCBs were 51pg TEQ g^{-1} lipid weight and 69pg TEQ g^{-1} lipid weight respectively, and none of the deer contaminant concentrations exceeded these levels (Figure 3.18).

Table 3.1 Mean organochlorine concentrations in ungulates.

Concentrations are reported in ng/g lipid weight unless otherwise specified. Ranges and standard errors are indicated in brackets.

Species	Region	Tissue	n	Fat %	∑PCB	HCB	Reference
Deer	Quebec	Fat	43	92	6.2 (0.7-35) [j]	2.2	Present Study
Deer	Quebec : control	Fat	33	93	4.0 (1.3-5.5) [j]	1.9	Present Study
Reindeer	Finland	Fat	10	-	3.5 (±8.8) [h]	-	Hirvi and Henttonen (2002)
Caribou	NWT (5 sites)	Fat	58	45.5 -85.6	16.5 (±5) [a]	72.3 (±19.3)	Elkin and Benthke (1995)
	NWT (2 sites)	Fat	2	na	38.3 (±13.7) [i]	66 (±18.8) [i]	Thomas and Hamilton (1988)
	NWT	Liver	1	na	8 [i]	1 [i]	Thomas and Hamilton (1988)
	NWT	Muscle	1	na	2 [i]	2 [i]	Thomas and Hamilton (1988)
	NWT Broughton Island	Fat	1	75.8	43 [f]	23 [i]	Muir et al. (1988[2])
	NWT Broughton Island	Muscle	1	2.2	10 [fi]	1.2 [i]	Muir et al. (1988[2])
	NWT Prince of Wales Island	Liver	na	na	<0.15 [ig]	0.93 [i]	Thomas et al. (1992)
	NWT Saglek Bay	Muscle	8	na	(0.14 – 17) [ij]	-	Gregor et al. (2003)
	NWT Saglek Bay	Fat	8	71	(10 – 514) [j]	-	
Deer	Alberta	Liver	14	3.2	(158-2799) [bj]	-	Gabos et al . (1998)
Whitetail		Muscle	14	1.87	(ND-1527) [bj]	-	Gabos et al . (1998)
Roe and red	Northern Poland	Fat	50	na	32 [c]	10	Falandysz and Kannaan (1992)
Fallow,red	Donana Spain	Muscle	8	na	96 (40-180) [i]	-	Hernandez et al. (1985)
Roe	Poland	Fat	10	na	4	-	Zasadowski et al. (2003)
Roe	Germany	Liver	35	na	150 [d]	20	Holm (1993)
Roe	Northern Italy	Muscle	25	68	11.2 [e]	1.7	Naso et al. (2004)

[a] ∑PCB Sum of 43 individual congeners
[b] ∑PCB Sum of 44 individual congeners
[c] ∑PCB Sum of 12 individual congeners
[d] ∑PCB Sum of PCB-138, PCB-153, PCB-180
[e] ∑PCB Sum of PCB-28, PCB-52, PCB-101, PCB-118, PCB-138, PCB-153, PCB-180
[f] ∑PCB Sum of 51 congeners
[g] Sum of PCBs-138 and -180
[h] ∑PCB Sum of 15 congeners (PCB-8, 15, 28, 52, 101, 114, 118, 128, 138, 141, 149, 151, 153, 170, 180)
[i] ng/g wet weight
[j] Measured in the vicinity of a point source. Concentrations in mammals both near and in remote locations from the source are included in the range.

Table 3.2 Mean relative abundance of PCB homologues and select congeners in deer.

Relative abundances in the 2002 deer are calculated as a % of total PCBs. These are expressed as an average of total (n=43), an average of deer samples located near (<5km, n=10) and far from the smelter (>15km, n=15). Standard errors are shown. Select PCB congeners are listed in order of descending abundance, and are separated in two groups showing those congeners where abundance 'near' exceeds 'far', and vice versa.

	Average of total	Near	Far
PCB Homologue Group			
mono+di-CB	1.11±0.25	0.45±0.20	2.05±0.77
tri-CB	10.50±0.99	7.40±0.48	12.50±2.34
tetra-CB	11.23±0.87	8.34±1.37	14.14±1.75
penta-CB	18.70±2.18	18.15±4.22	19.12±2.69
hexa-CB	31.65±05.52	34.06±11.97	29.20±5.99
hepta-CB	16.66±4.75	19.53±11.03	14.57±4.57
octa-CB	7.13±1.33	9.34±2.53	5.02±1.06
nona-CB	2.13±0.61	2.19±1.26	2.52±1.20
deca-CB	0.89±0.16	0.54±0.23	0.88±0.42
PCB Congeners			
153-132-105	14.55±3.36	15.60±7.74	14.87±3.37
138-163	7.63±1.95	9.87±4.45	6.54±1.16
180	7.13±2.40	8.54±5.55	6.70±2.68
157-200	4.04±1.43	6.58±2.82	1.35±1.2
170-190	3.16±1.10	3.67±2.41	2.49±1.26
201	2.39±0.48	3.09±1.01	1.90±0.31
101	2.19±0.35	2.47±0.60	1.45±0.39
85	1.50±0.29	1.05±0.24	1.50±0.32
156-202-171	1.43±0.30	1.63±0.64	1.32±0.36
187-182	1.40±0.33	1.69±0.74	0.95±0.23
207	1.14±0.59	1.45±1.32	1.42±0.98
193	0.58±0.12	0.71±0.16	0.54±0.23
31-28	3.54±0.42	2.65±0.54	4.05±0.85
15-17	2.22±0.49	0.90±0.41	4.09±1.54
74	1.76±0.15	1.19±0.12	2.06±0.39
43	1.37±0.26	0.70±0.15	2.30±0.91
66	1.17±0.17	0.79±0.22	1.14±0.33
16-32	0.66±0.16	0.30±0.09	0.75±0.43

Table 3.3 Results for the regression and an ANCOVA between PCB concentration and distance from the smelter in deer from 1999 and 2002.

The coefficients of determination (r^2), slopes for the lines of best fit (m), and intercepts are shown for the regression between log concentration (pg g^{-1} wet weight) and distance (km) from the smelter in the 1999 control (n=33) and 2002 (n=43) samples. Individual regressions were run for both 1999 and 2002 individuals, and if detected, a significant decline with distance is indicated in the r^2 column. An ANCOVA model indicated whether the slopes (m) were significantly different between the 1999 and 2002 individuals (year*distance interaction), and significance in this model, if detected, is indicted beside the 2002 slope (m). Significance is reported at the 95% confidence level: *($p<0.05$); **($p<0.01$); ***($p<0.001$).

	1999			2002		
OC Compound	r^2	m	Intercept	r^2	m	Intercept
PCB Homologue						
Mono and Dichlorinated	0.000	-0.001	1.77	0.003	0.009	1.75
Trichlorinated	0.040	0.007	2.55	0.033	-0.008	2.79
Tetrachloinated	0.007	-0.003	2.75	0.042	-0.007	2.84
Pentachlorinated	0.008	0.003	2.85	0.18**	-0.019*	3.15
Hexachlorianted	0.005	0.002	2.93	0.218**	-0.021**	3.38
Heptachlroinated	0.005	-0.002	2.69	0.215**	-0.033*	3.11
Octachlorinated	0.000	0.000	2.53	0.068*	-0.009*	2.79
Nonachlorinated	0.005	-0.002	1.88	0.018	-0.006	2.10
Decachlorinated	0.003	0.003	1.31	0.030	-0.011	1.57
∑PCB	0.003	0.001	3.55	0.214**	-0.017**	3.87

	1999			2002		
OC Compound	r^2	m	Intercept	r^2	m	Intercept
PCB Congener						
31-28	0.025	0.009	1.96	0.006	0.004	2.24
52	0.008	-0.004	1.60	0.047	-0.010	1.95
74	0.016	-0.004	2.08	0.017	-0.007	1.99
99	0.017	0.005	1.96	0.096*	-0.017*	2.15
101	0.051	0.014	1.76	0.278***	-0.035**	2.32
118	0.008	0.004	2.23	0.048	-0.011	2.43
153-105-132	0.001	0.001	2.64	0.074*	-0.011	2.90
133	0.004	0.004	1.82	0.108*	-0.012	2.26
138-163	0.014	0.005	2.22	0.136*	-0.017*	2.67
187-182	0.050	0.015	1.27	0.234**	-0.028**	2.06
177	0.001	0.001	1.46	0.078*	-0.013	1.77
180	0.041	-0.007	2.42	0.052	-0.013	2.49
193	0.003	0.003	1.31	0.138*	-0.025*	1.67
201	0.000	0.001	1.85	0.207**	-0.026**	2.37
209	0.003	0.003	1.31	0.030	-0.011	1.69

Table 3.4 Bioconcentration factors (BCF) and relative abundance of individual PCDD/F congeners in deer and smelter emissions.

Relative abundances are expressed as a % of total PCDD/Fs. A ratio of congener abundances from deer to air represents the transfer of individual PCDD/F congeners to the deer

PCDD/Fs	BCF[a]	%Abundance (pgTEQ g^{-1}) in deer	% Abundance (pgTEQ) in smelter emissions	Deer: Air ratio
2378-TCDF	0.94	1.77	12.32	0.14
12378-PeCDF	0.73	1.47	8.76	0.17
23478-PeCDF	3.1	22.47	19.99	1.12
123478-HxCDF	2.34	3.74	28.77	0.13
123678-HxCDF	2	3.65	7.72	0.47
123789-HxCDF	2	5.07	1.32	3.86
234678-HxCDF	1.78	4.88	2.75	1.77
1234678-HpCDF	0.41	0.38	2.80	0.14
1234789-HpCDF	0.99	0.45	0.92	0.49
OCDF	0.2	0.01	1.42	0.01
2378-TCDD	4.32	6.62	3.52	1.88
12378-PeCDD	4.16	36.06	4.95	7.29
123478-HxCDD	2.02	4.82	0.80	6.00
123678-HxCDD	1.74	3.69	1.77	2.09
123789-HxCDD	2.24	4.46	1.39	3.21
1234678-HpCDD	0.36	0.45	0.66	0.68
OCDD	0.52	0.01	0.16	0.07

[a] BCF: beef bioconcentration factor, unitless. Obtained from an air-beef food chain model by Lorber et al. (1994)

Table 3.5 Results for the regression between PCDD/F and coplanar PCB concentrations and distance from the smelter in deer from 2002.

The coefficients of determination r^2 , slopes for the lines of best fit (m), and intercepts are shown for the regression between log concentration (pg g^{-1} wet weight) and distance (km) from the smelter (n=12). Significance is reported at the 95% confidence level.* ($p<0.05$)

	r^2	m	Intercept
PCDD/Fs			
2378-TCDF	0.02	-0.004	0.24
12378-PeCDF	0.074	-0.009	0.39
23478-PeCDF	0.101	-0.012	0.52
123478-HxCDF	0.075	-0.01	0.45
123678-HxCDF	0.075	-0.01	0.44
123789-HxCDF	0.068	-0.01	0.52
234678-HxCDF	0.07	-0.01	0.49
∑ HxCDF	0.07	-0.015	0.876
1234678-HpCDF	0.072	-0.018	0.133
1234789-HpCDF	0.074	-0.011	0.483
OCDF	0.083	-0.023	0.59
∑PCDFs	0.067	-0.02	1.192
2378-TCDD	0.16	-0.005	0.168
12378-PeCDD	0.119	-0.012	0.466
123478-HxCDD	0.101	-0.014	0.365
123678-HxCDD	0.12	-0.013	0.462
123789-HxCDD	0.07	-0.011	0.48
∑ HxCDD	0.106	-0.015	0.84
1234678-HpCDD	0.064	-0.015	0.21
OCDD	0.115	-0.018	0.682
∑PCDDs	0.122	-0.012	1.14
∑PCDD/Fs	0.095	-0.02	1.487
no-PCBs			
PCB 77	0.2	-0.027	2.14
PCB 126	0.39*	-0.03	1.41
PCB 169	0.30*	-0.03	0.802
∑no-PCBs	0.37*	-0.026	1.64

Table 3.6 Comparison of deer portions required per week to exceed WHO (1998) - 1 - 4 pg TEQ kg^{-1} bw day^{-1}- safety levels[a] in adults.

Contaminant levels from samples are presented and grouped due to varying distances from the smelter. Lipid content in deer muscle was approximated at 1.87%[b]. The weekly meat portion (227g)[c] was corrected for lipid content, resulting 4.25g lipid content per portion. Estimates are calculated for an adult (70 kg)[c].

Sample pool	∑PCDD/Fs + ∑no-PCBs (pg TEQ.g^{-1})	∑PCDD/Fs + ∑no-PCBs (pgTEQ.$portion^{-1}$)	Single portion intake of ∑no-PCBs+∑PCDD/Fs (pg TEQkg^{-1} bw $week^{-1}$)	# portions to exceed WHO 7 -28 pgTEQkg^{-1}bw wk^{-1}	# portions to exceed Health Canada 70pg TEQ kg^{-1} bw $month^{-1}$
Max. value	38.79	164.86	2.36	3 - 11	30
< 5km[d]	11.19	47.56	0.68	10 - 40	102
5-20km[e]	5.31	22.61	0.32	22 - 88	219
>20km[f]	1.15	4.93	0.07	100 - 400	1000
Avg[g]	7.56	32.13	0.46	15 - 60	152

[a] Calculations based on Easton et al. (2002)
[b] Value adopted from Gabos et al. (1998) and laboratory tests on deer muscle tissue
[c] Based on Health Canada (1994), and Hites et al. (2004)
[d] Mean of sample with 5 km of source. n=6: sample ID #'s 573,519, 560, 571, 502, 501
[e] Mean of sample beyond 5km and within 20kmn of source. n=4: sample ID#'s 569, 555, 577, 570
[f] Mean of sample beyond 20 km of source. n=2: sample ID#s 509, 566
[g] Mean of all samples n=12

Table 3.7 Comparison of deer portions required per week to exceed WHO (1998) - 1 - 4 pg TEQ kg^{-1} bw day^{-1}- safety levels[a] in toddlers and children.

Contaminant levels from samples are presented and grouped due to varying distances from the smelter. Lipid content in deer muscle was approximated at 1.87%[b]. The weekly meat portion was corrected for lipid content. Estimates are calculated for toddlers (7 months-4 years; 13kg; 85g portion) and children (5-11 years; 27kg; 125g portion)[c].

Sample pool	∑PCDD/Fs + ∑no-PCBs (pg TEQ.g^{-1})	Single portion intake of ∑no-PCBs+∑PCDD/Fs (pg TEQkg^{-1} bw $week^{-1}$) Toddlers	Single portion intake of ∑no-PCBs+∑PCDD/Fs (pg TEQkg^{-1} bw $week^{-1}$) Children	# portions to exceed WHO 7 -28 pgTEQkg^{-1}bw wk^{-1} in toddlers; children	# portions to exceed Health Canada 70pg TEQ kg^{-1} bw $month^{-1}$ in toddlers; children
Max. value	38.79	4.74	3.40	1.5 – 6 ; 2 - 8	14 ; 20
< 5km[d]	11.19	1.36	0.97	5– 20 ; 7 - 28	51 ; 72
5-20km[e]	5.31	0.65	0.46	10 - 43 ; 15 -60	107 ; 152
>20km[f]	1.15	0.14	0.10	50 - 200 ; 70 -280	500 ; 700
Avg[g]	7.56	0.92	0.66	7 - 30 ; 10- 42	76 ; 106

[a] Calculations based on Easton et al. (2002)
[b] Value adopted from Gabos et al. (1998) and laboratory tests on deer muscle tissue
[c] Based on Health Canada (1994)
[d] Mean of sample with 5 km of source. n=6: sample ID #'s 573,519, 560, 571, 502, 501
[e] Mean of sample beyond 5km and within 20kmn of source. n=4: sample ID#'s 569, 555, 577, 570
[f] Mean of sample beyond 20 km of source. n=2: sample ID#s 509, 566
[g] Mean of all samples n=12

Table 3.8 Toxic equivalent (TEQ) concentrations (pg/g whole weight) of dioxin-like chemicals in fatty foods from Montreal[a] compared to deer.

Contaminant levels in deer are grouped according to varying distances from the smelter: deer with maximum contaminant value (within 5km and in the prevailing wind direction) (n=1), deer <5km (n=6), deer between 5-20km (n=4), deer beyond 20km (n=2).

Description	TEQ concentration (pg/g whole wt)	Description	TEQ concentration (pg/g whole wt)
Maximum value deer	0.725	Lunch meat canned	0.075
Butter	0.614	Lamb	0.066
Freshwater fish	0.481	Formula milk	0.065
Shell fish	0.451	Eggs	0.063
Organ meat	0.417	Ice cream	0.062
Ground beef	0.383	Poultry	0.062
Cheddar cheese	0.357	Evaporated milk	0.061
Cooking fat	0.331	Fish burger	0.061
Wieners	0.288	Baby dinner	0.051
Fish canned	0.225	Pork cured	0.049
Processed cheese	0.218	Veal	0.041
Deer (< 5 km)	0.209	Whole milk	0.04
Margarine	0.183	Frozen entree	0.028
Hamburger	0.183	Pork fresh	0.025
Beef steak	0.181	Baby dinner	0.025
Beef roast	0.157	2% milk	0.024
Cream	0.138	1% milk	0.024
Pizza	0.13	Frozen dinner	0.023
Marine fish	0.118	Deer (>20km)	0.022
Deer (5-20km)	0.099	Yogurt	0.019
Baby food meat	0.091	Skim milk	0.013
French fries	0.084	Meat soup	0.013
Cottage cheese	0.079	Dehydrated soup	0.008
Cold cuts	0.079		

[a]Health Canada 1993[1]

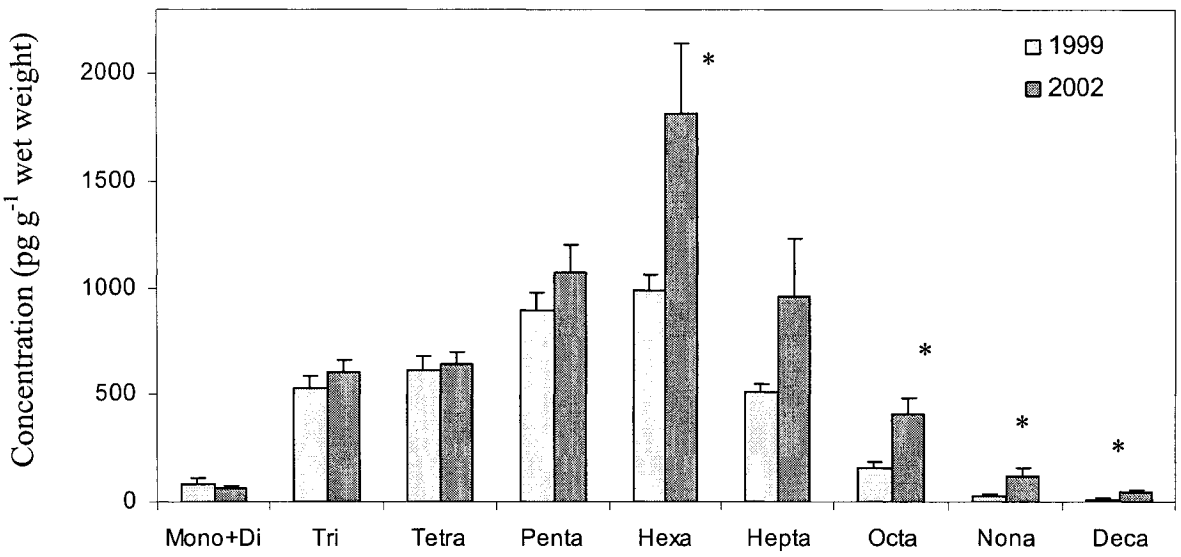


Figure 3.1 Mean concentrations of PCB homologues in deer from 1999 and 2002.

Mean PCB homologue concentrations of deer from Danville in 1999 (n=33) and 2002 (n=43) are given in pg/g wet weight. Significant differences between the years ($P<0.05$) are indicated with an asterisk.

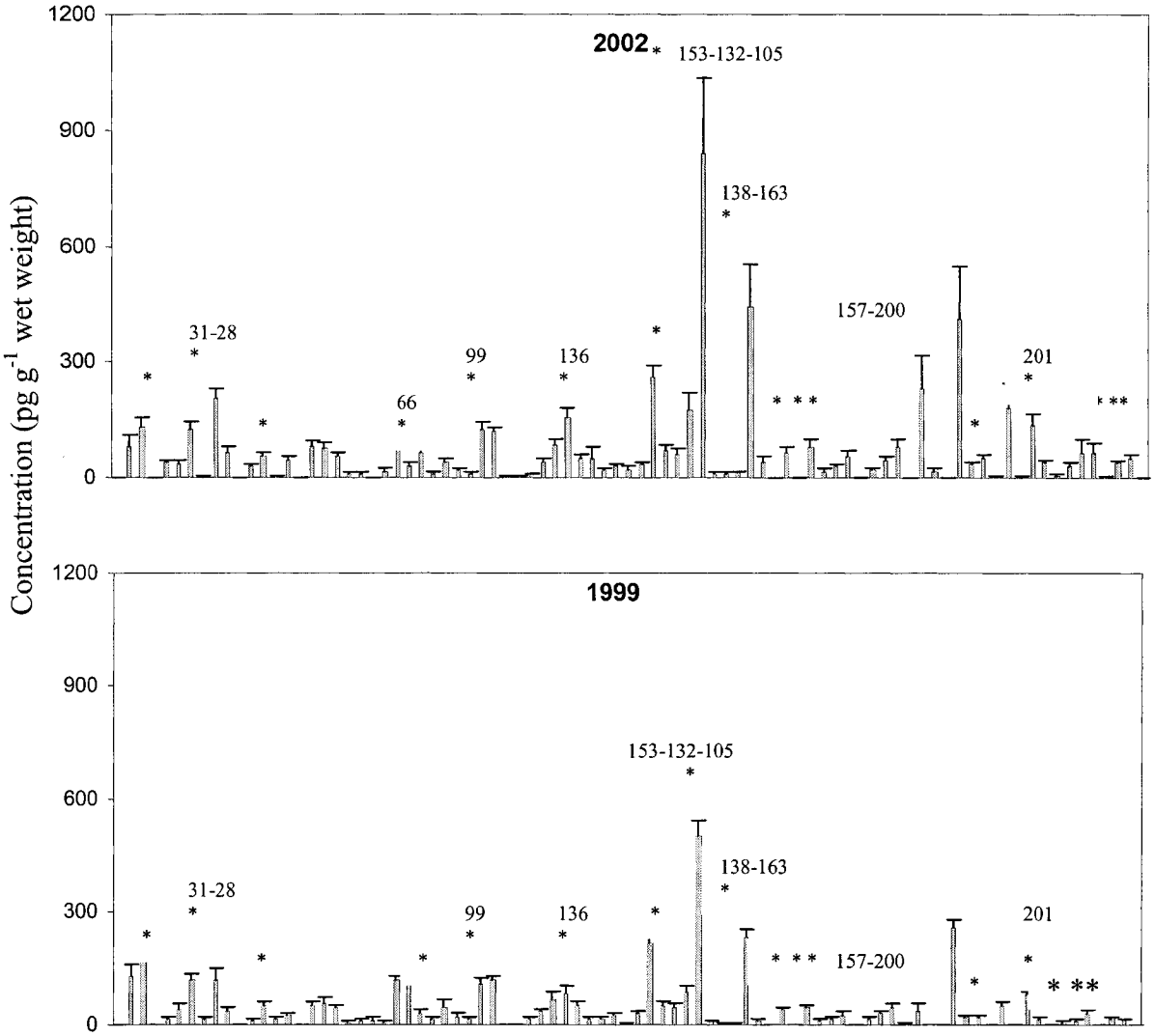


Figure 3.2 Mean concentrations of PCB congeners in deer from 1999 and 2002.

Mean PCB homologue concentrations of deer from Danville in 1999 (n=33) and 2002 (n=43) are given in pg/g wet weight. Significant differences between the years ($P<0.05$) are indicated with an asterisk.

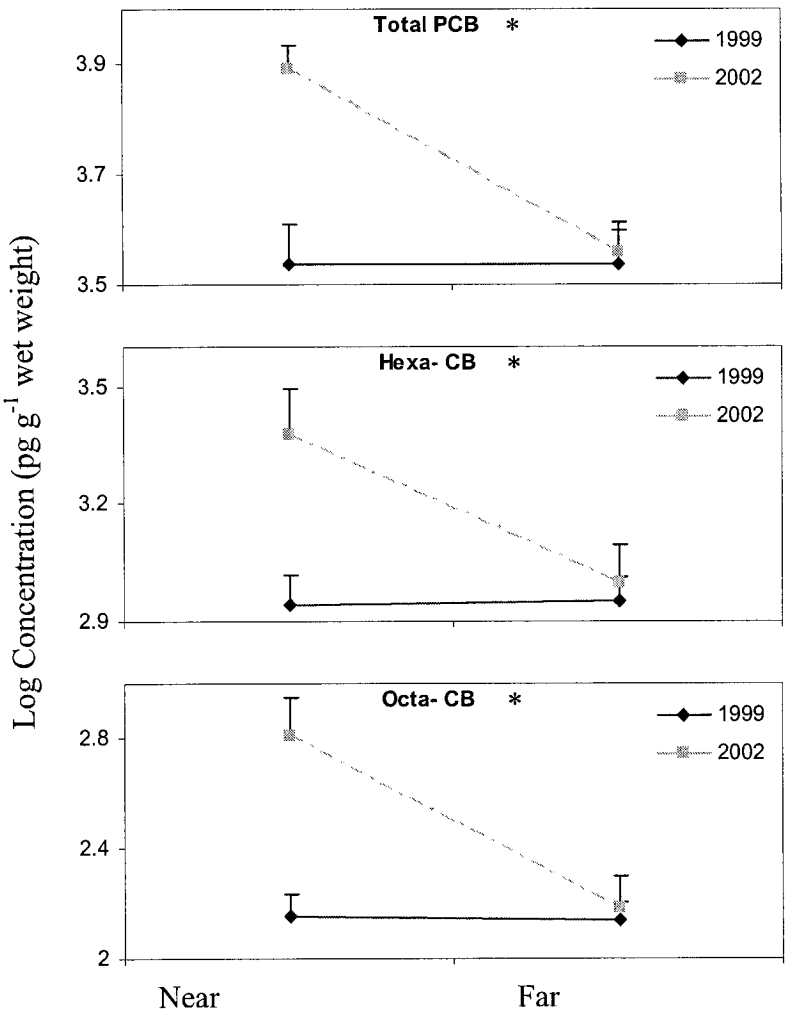


Figure 3.3 Concentration of Total PCBs, hexachlorobiphenyls, and octachlorobiphenyls in deer near (<5km) and far (>15km) from the smelter in 1999 and 2002.

Using a BACI design, a 2-way ANOVA was used to test each factor (distance and year), indicating whether mean homologue concentrations were significantly different between 1999 and 2002 (year), and between the two distance groups ('near' <5km and 'far' >15km) (distance), and the interaction (year*distance). Significance is reported if both factors and the interaction term are significant at the 95% confidence level ($P<0.05$), and is denoted by an asterisk. Sample sizes are as follows: (n=9) for samples in 1999 and near, 1999 and far (n=12), 2002 and near (n=10), 2002 and far (n=15).

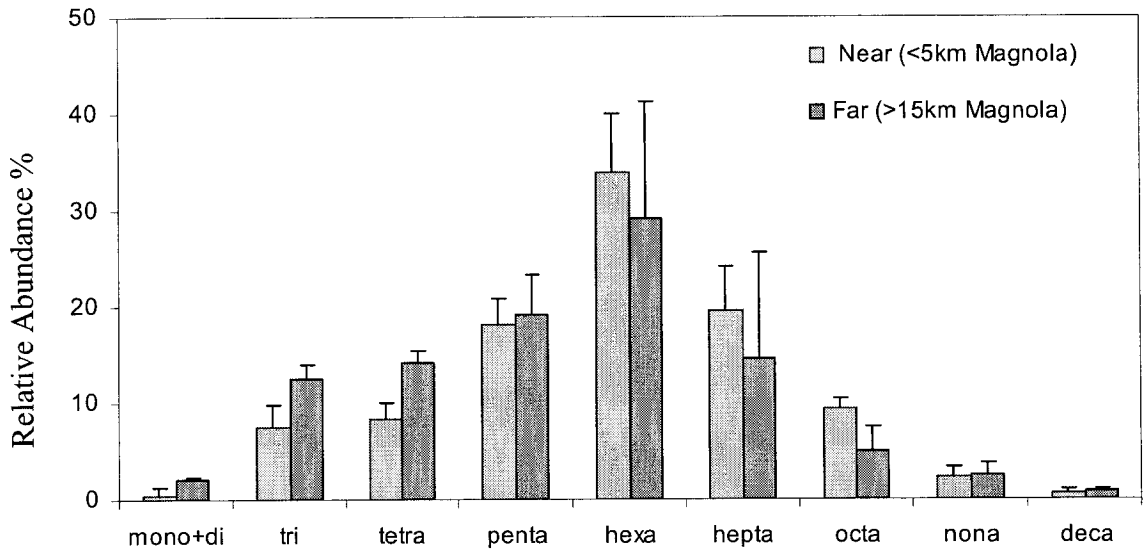


Figure 3.4 Relative abundance of PCB homologue groups in deer near (<5km) and far (>15km) from the smelter in 2002.

Relative abundance is expressed as a % of total PCBs. Standard error bars are shown. Sample sizes are as follows: (n=10) for near, (n=15) for far.

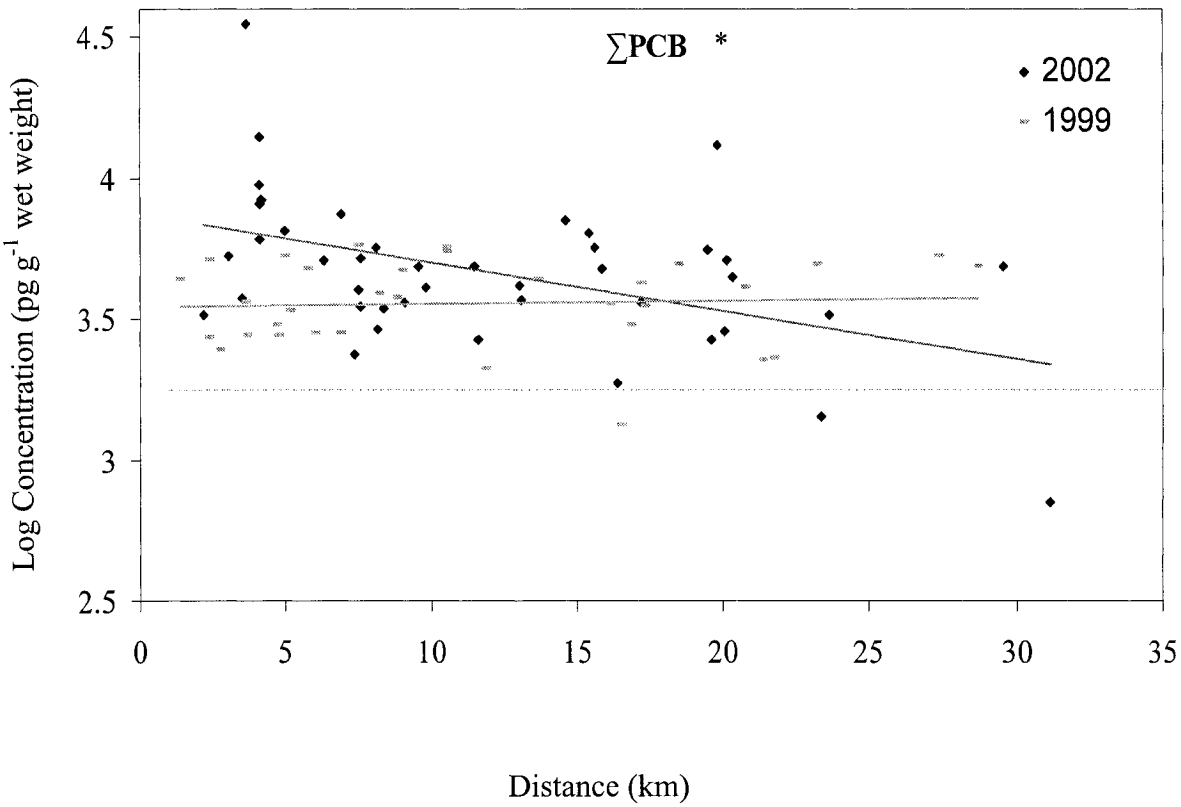


Figure 3.5 Relationship between total PCB concentration and distance in deer from 1999 and 2002.

Points represent the log concentration (pg g^{-1} wet weight) of each deer at a specified distance (km) from the smelter. Diamonds represent 2002 (n=43) and Dashes 1999 (n=33). Lines of best fit were drawn for both years. Significance was denoted with an asterisk (*$p<0.05$) if the regression in 2002 was significant, and if slopes were significantly different between 1999 and 2002 as tested by an ANCOVA (year*distance interaction term). The detection limit is indicated by a dotted line.

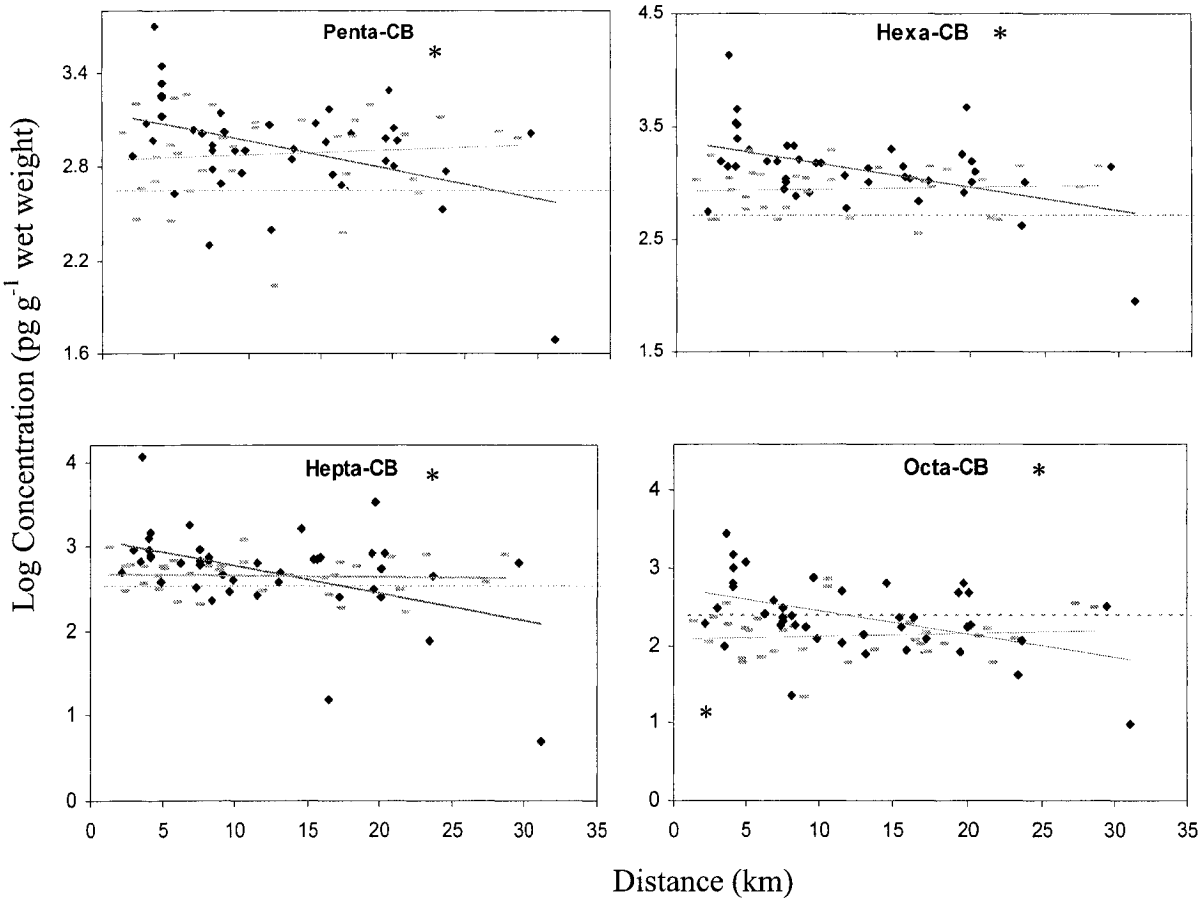


Figure 3.6 Relationship between PCB homologue group concentrations and distance in deer from 1999 and 2002.

Points represent the log concentration (pg g^{-1} wet weight) of each deer at a specified distance (km) from the smelter. Diamonds represent 2002 (n=43) and dashes 1999 (n=33). Lines of best fit were drawn for both years. Significance was denoted with an asterik (*$p<0.05$) if the regression in 2002 was significant, and if slopes were significantly different between 1999 and 2002 as tested by an ANCOVA (year*distance interaction). For octa-CB, all zero values were assigned randomly generated values that were between 0 and the detection limit. The detection limit is indicated by a dotted line.

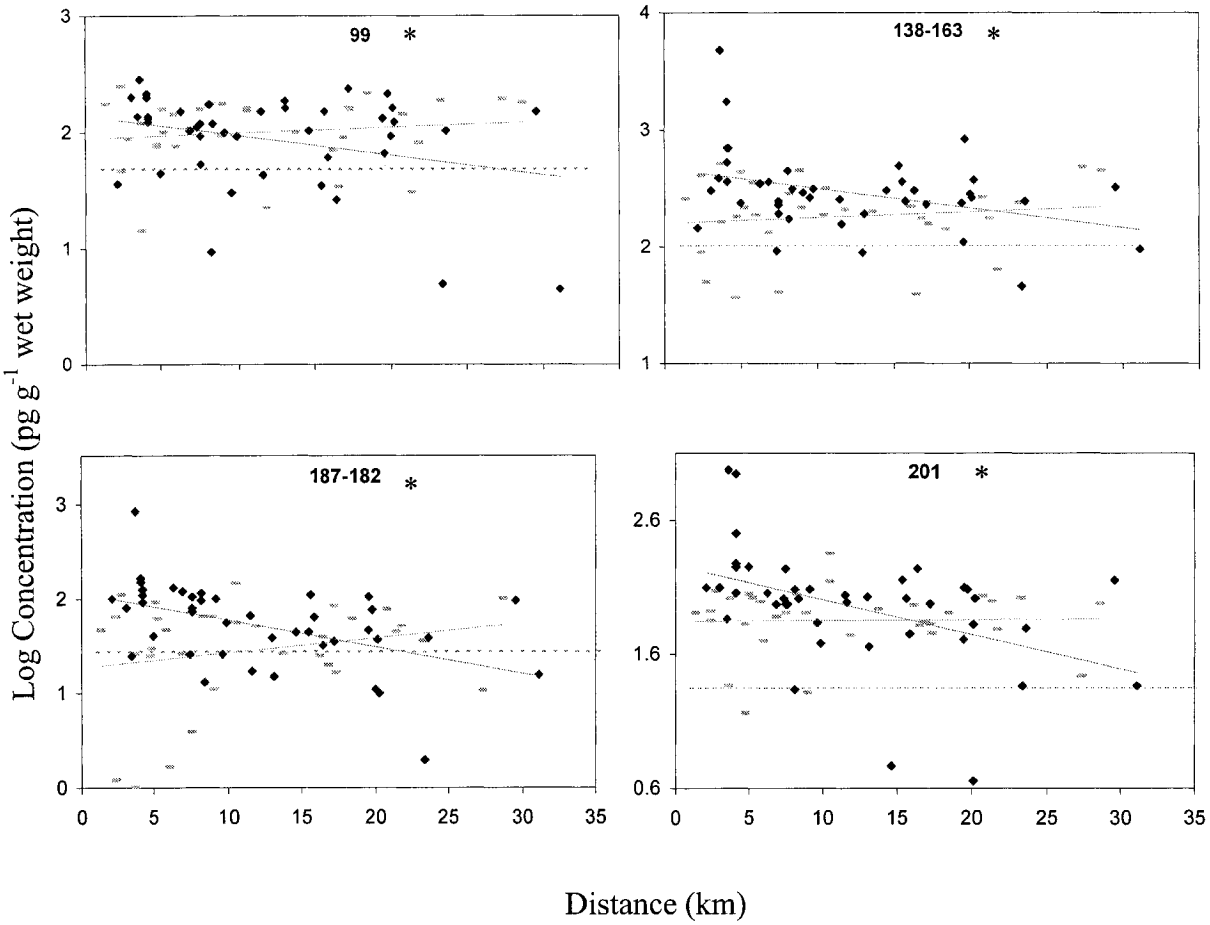


Figure 3.7a Relationship between select PCB congener concentrations and distance from the smelter in deer from 1999 and 2002.

Points represent the log concentration (pg g^{-1} wet weight) of each deer at a specified distance (km) from the smelter. Diamonds represent 2002 (n=43) and dashes 1999 (n=33). Lines of best fit were drawn for both years. Significance was denoted with an asterisk (*$p<0.05$) if the regression in 2002 was significant, and if slopes were significantly different between 1999 and 2002 as tested by an ANCOVA (year*distance interaction). All zero values were assigned randomly generated values that were between 0 and the detection limit. The detection limit is indicated by a dotted line.

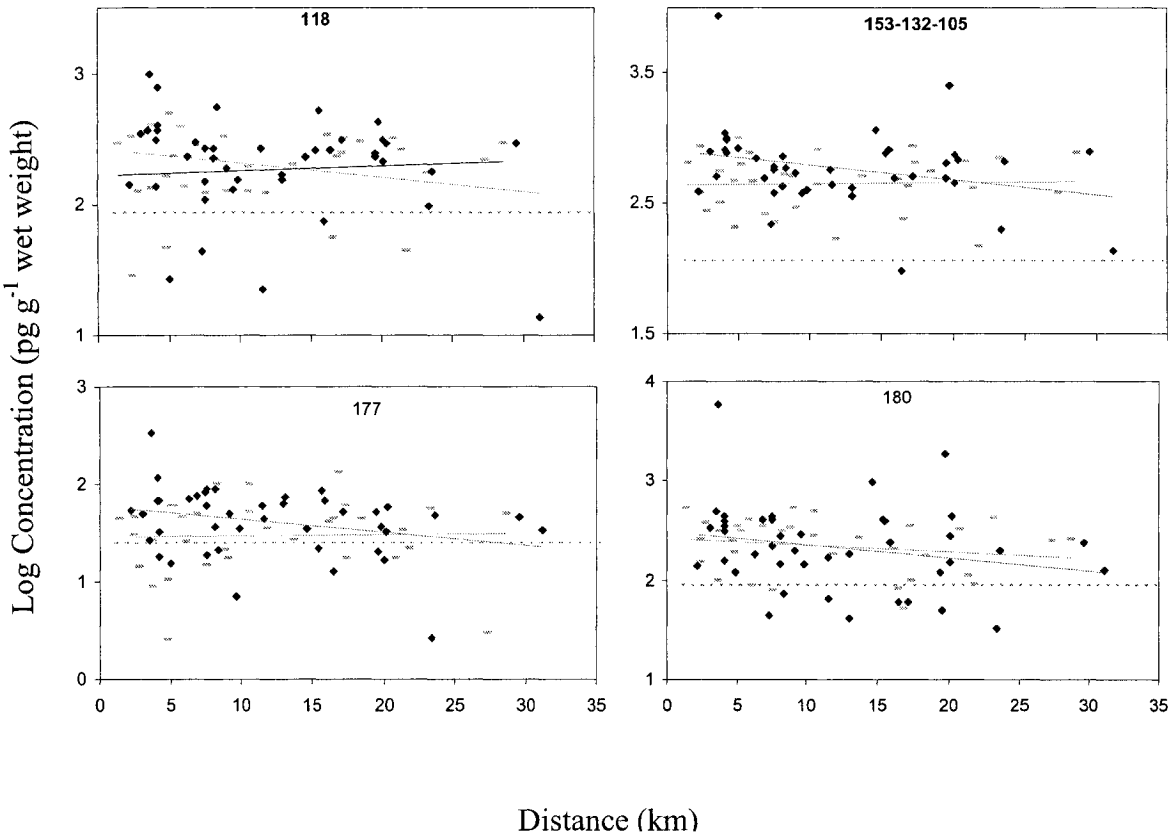


Figure 3.7b Relationship between select PCB congener concentrations and distance from the smelter in deer from 1999 and 2002.

Points represent the log concentration (pg g^{-1} wet weight) of each deer at a specified distance (km) from the smelter. Diamonds represent 2002 (n=43) and dashes 1999 (n=33). Lines of best fit were drawn for both years. All zero values were assigned randomly generated values that were between 0 and the detection limit. The detection limit is indicated by a dotted line.

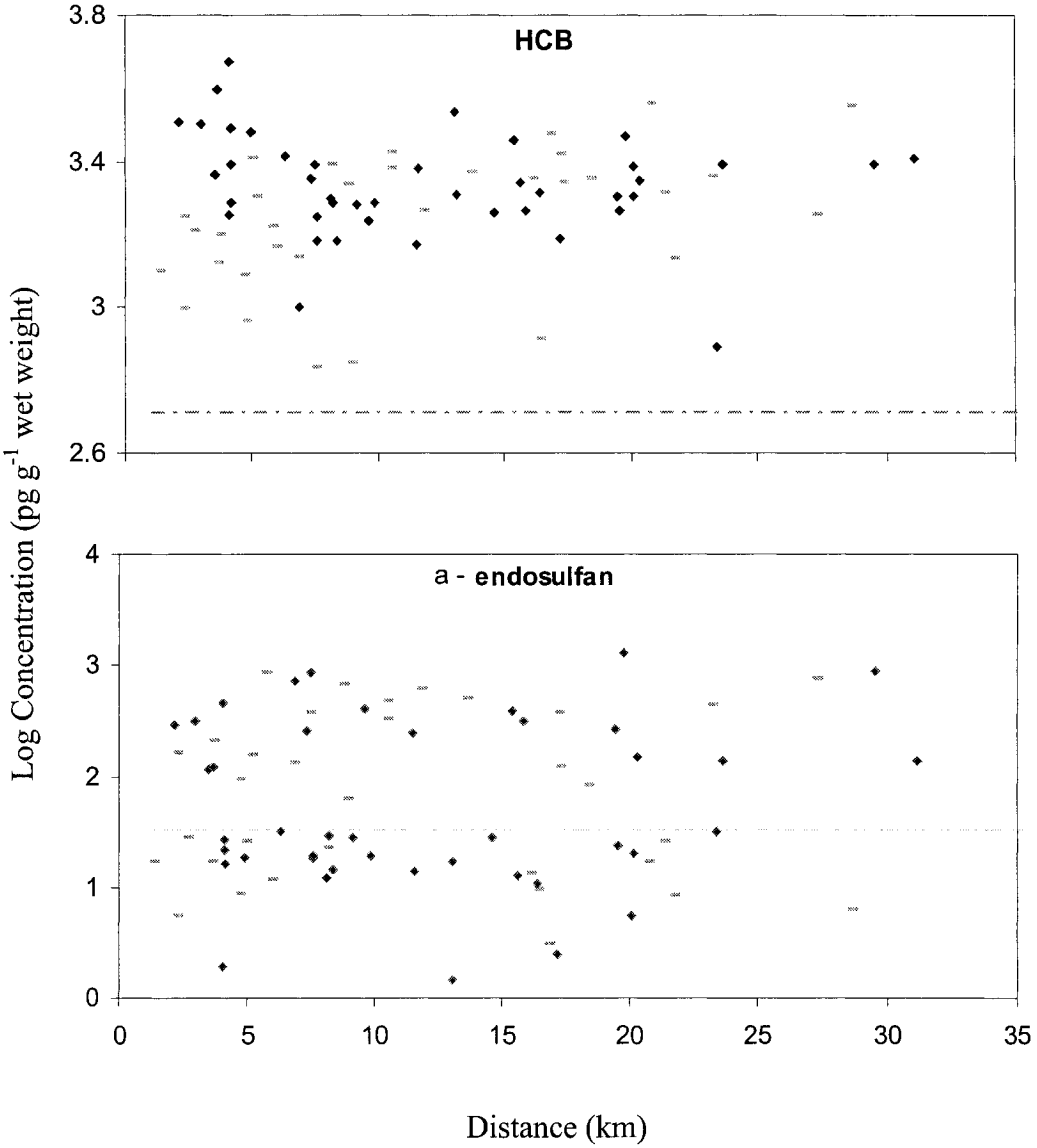


Figure 3.8 Relationship between organochlorine pesticide concentrations and distance from the smelter deer in 1999 and 2002.

Points represent the log concentration (pg g^{-1} wet weight) of each deer at a specified distance (km) from the smelter. HCB, an emission product, and a-endosulfan, a non-emission product, are shown. For a-endosulfan all zero values were assigned randomly generated values that were between 0 and the detection limit. Dotted lines show detection limits (DL) for each compound.

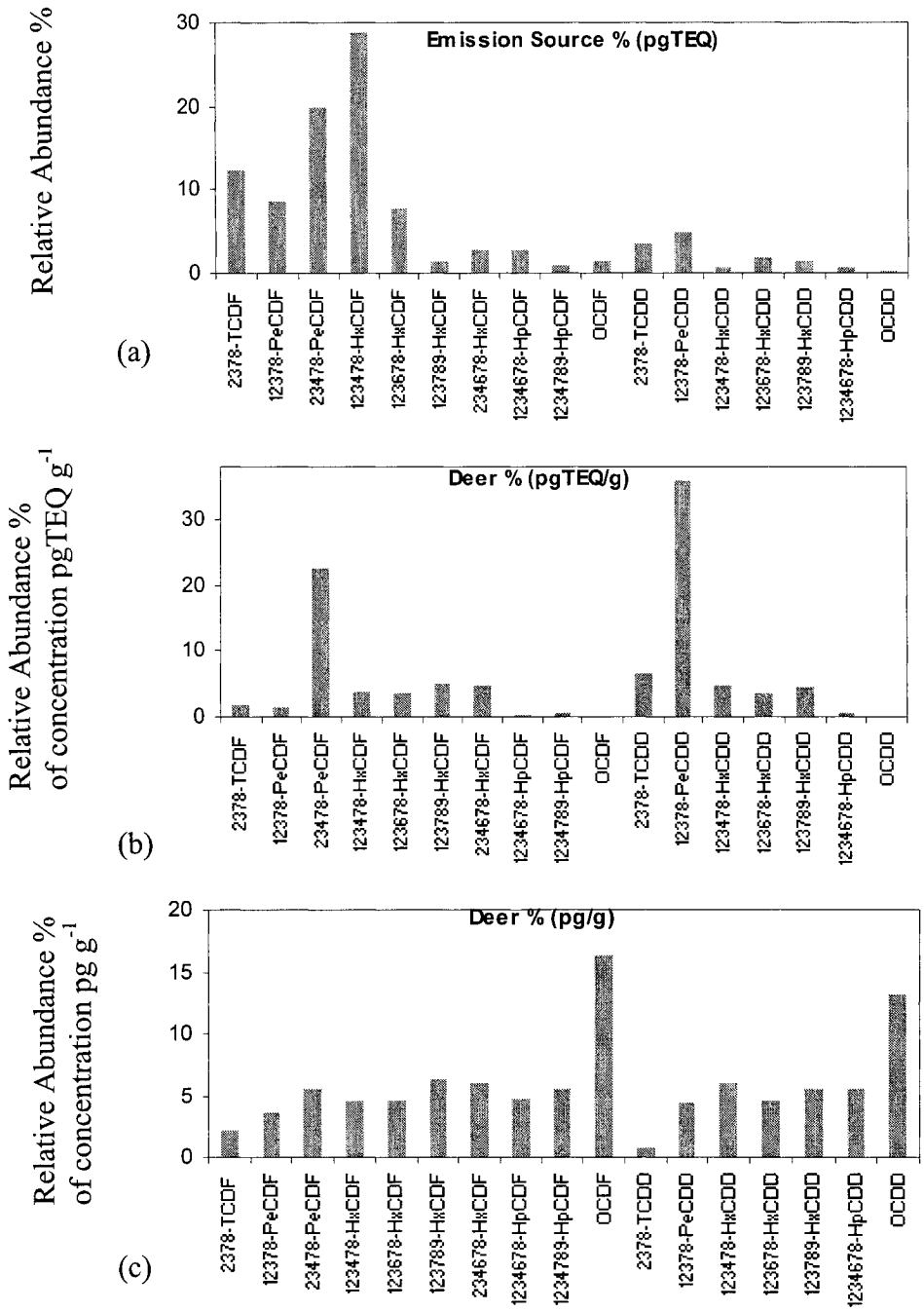


Figure 3.9 Relative abundance of PCDD/F congeners in the smelter and in deer.

The relative abundance of each congener is calculated as a % of total PCDD/Fs and is reported in: (a) smelter emissions (pgTEQ); (b) deer expressed from pgTEQ g^{-1} concentration; (c) deer expressed from pg g^{-1} concentration.

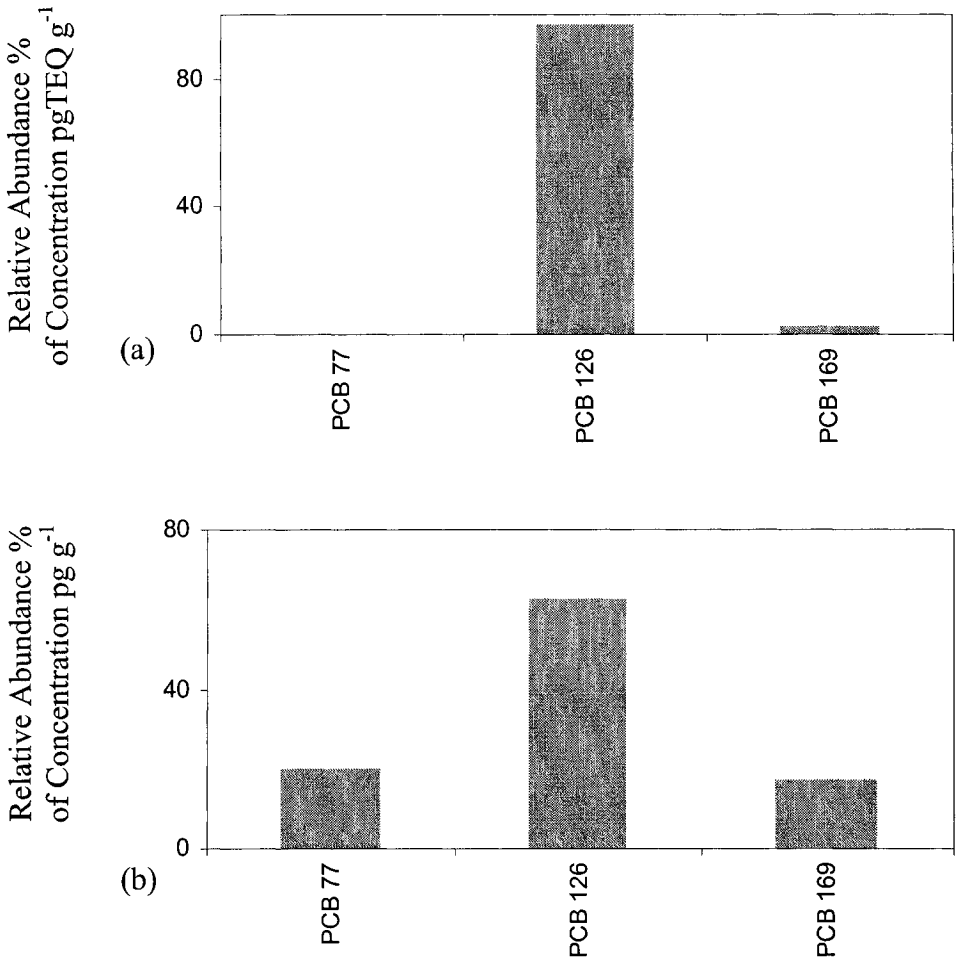


Figure 3.10 Relative abundance of coplanar PCBs in deer.

The relative abundance of each congener is expressed as a % total coplanar PCBs, from concentrations in (a) pgTEQ g^{-1}, and (b) pg g^{-1}.

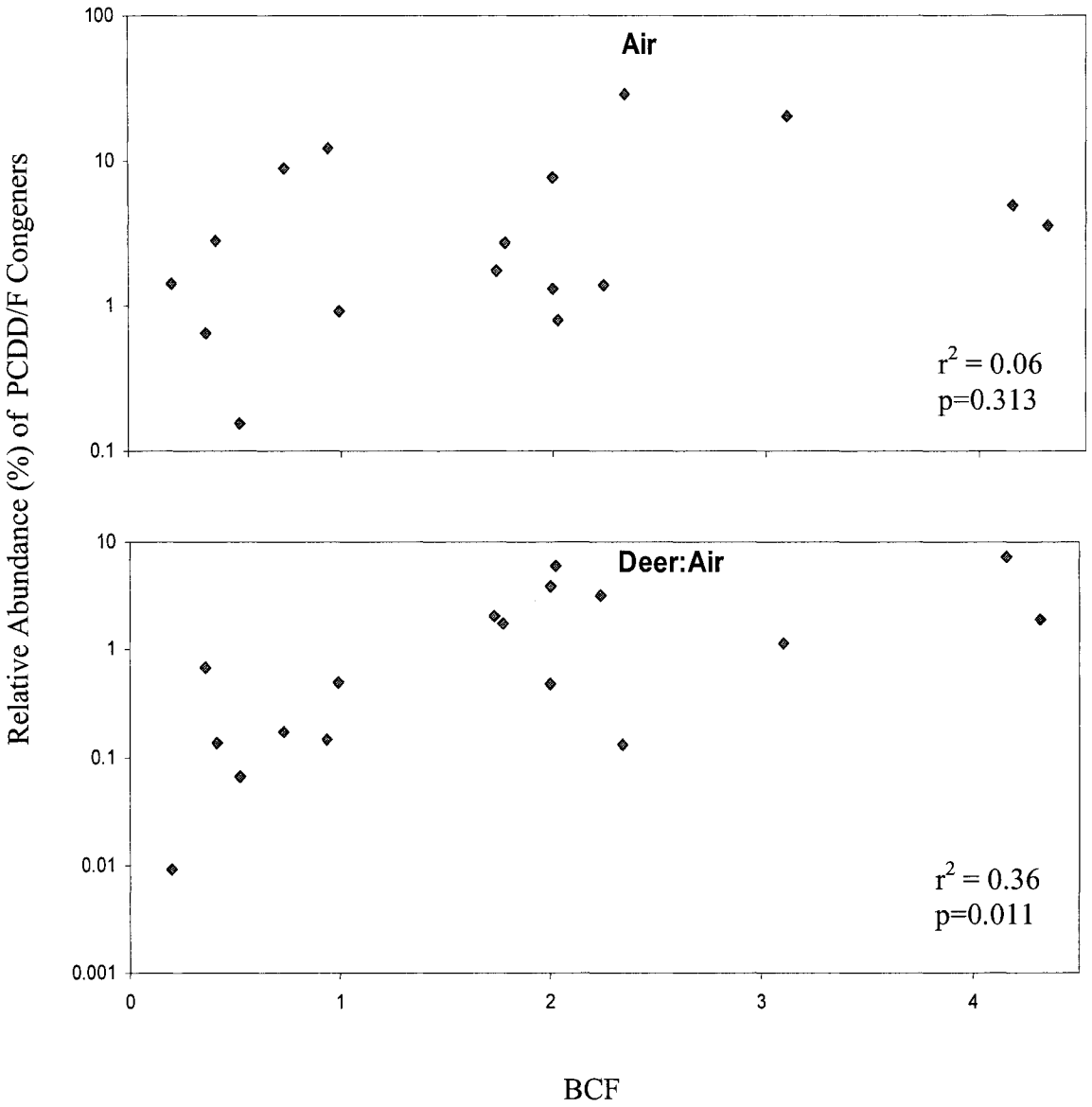


Figure 3.11 Relationship between BCF and relative abundance of PCDD/F congeners in air emissions, and expressed as a ratio in deer : air.

BCF: beef bioconcentration factor, unitless. Obtained from an air-beef food chain model by Lorber et al. (1994).

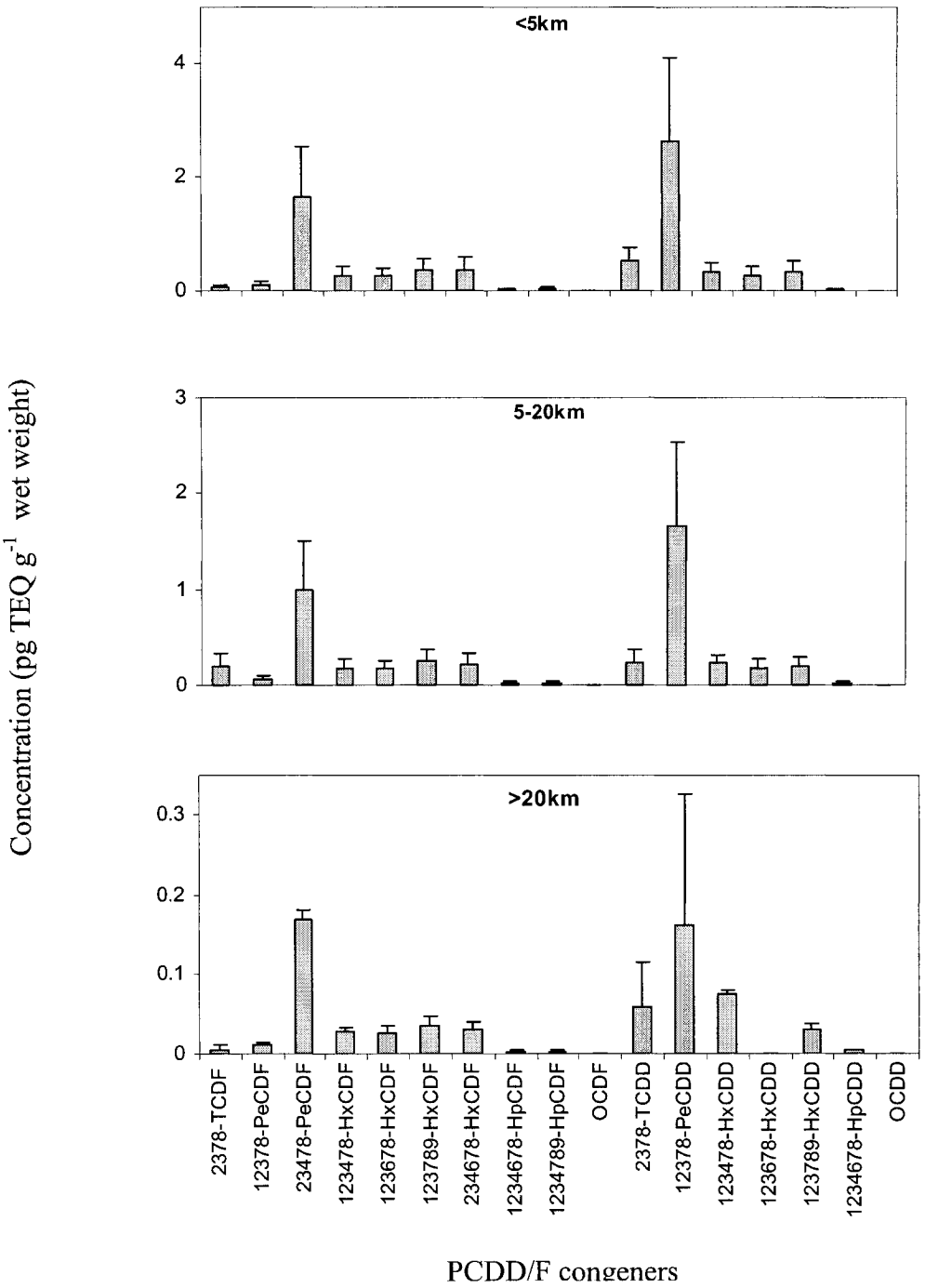


Figure 3.12 Congener profiles of PCDD/F concentrations in deer expressed in pgTEQ g^{-1} wet weight at varying distances from the smelter.

Samples (n=12) are grouped as follows: those within 5km (n=6), between 5-20km (n=4), >20km (n=2). Error bars are shown.

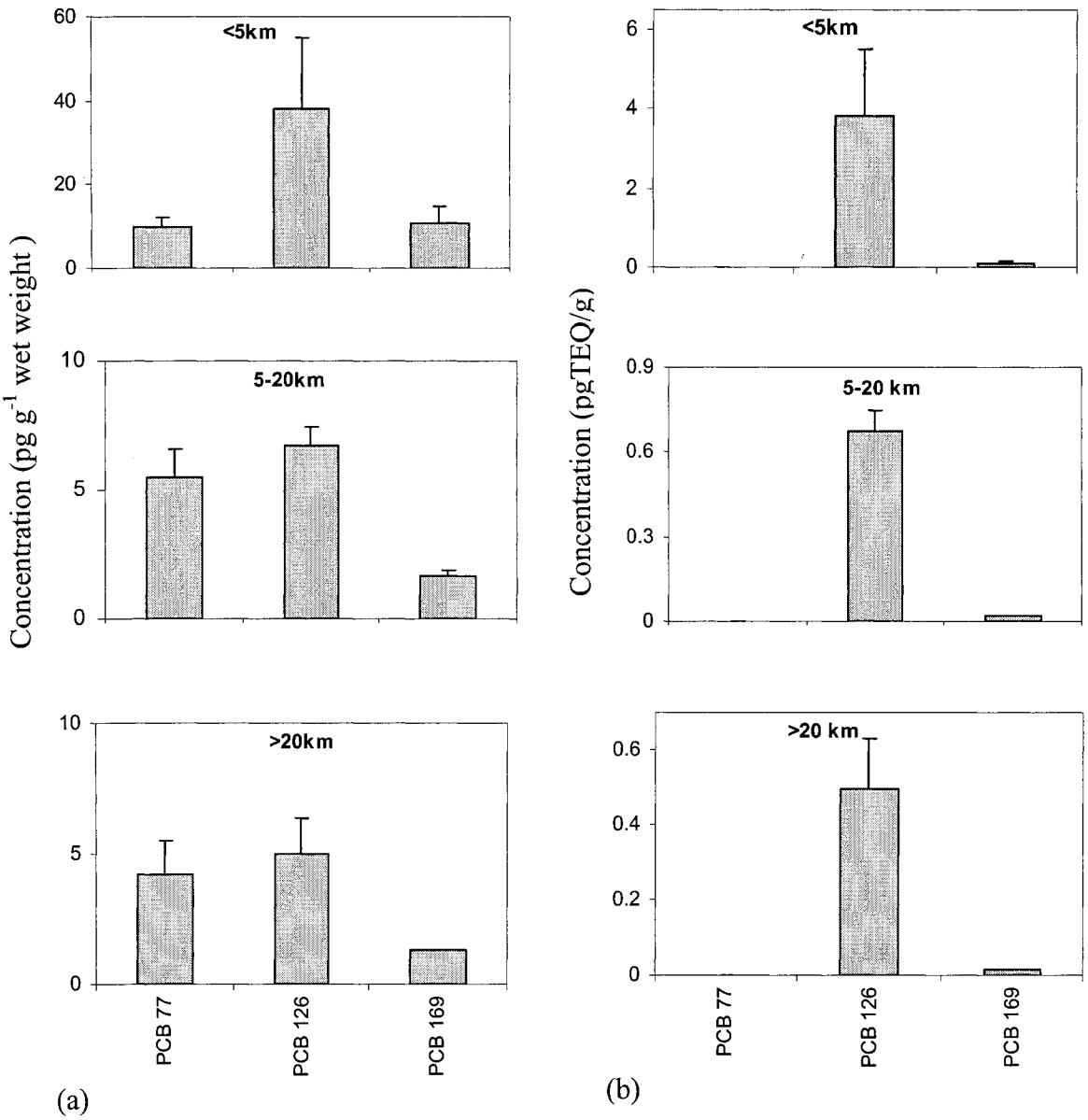


Figure 3.13 Congener profiles of coplanar PCB concentrations in deer at varying distances from the smelter.

Concentrations are expressed in (a) pg/g wet weight, and (b) pgTEQ g^{-1}. Samples (n=12) are grouped as follows: those within 5km (n=6), between 5-20km (n=4), >20km (n=2). Error bars are shown.

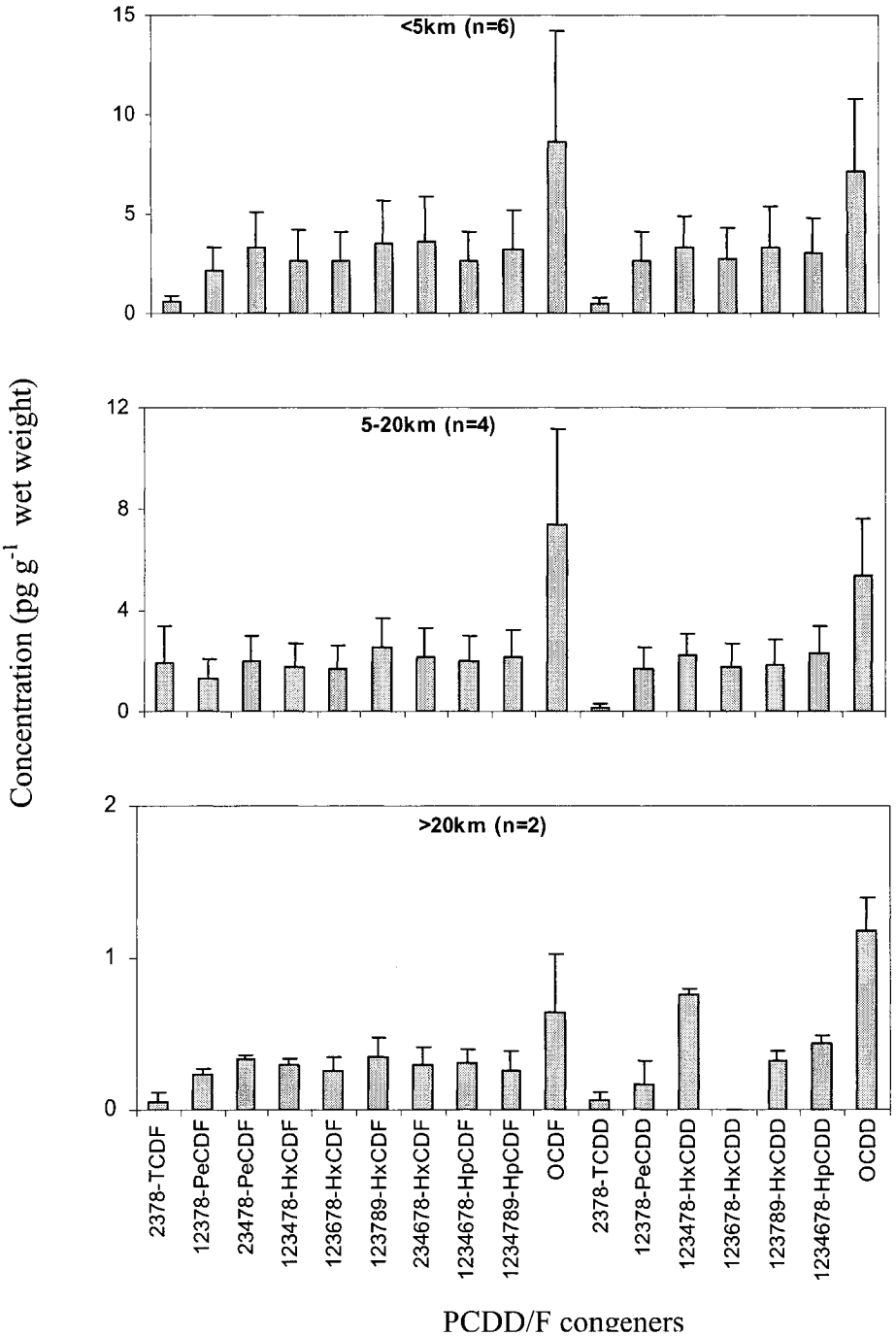


Figure 3.14 Congener profiles of PCDD/F concentrations in deer expressed in pg/g wet weight at varying distances from the smelter.

Samples (n=12) are grouped according to distance from the smelter: within 5km (n=6), between 5-20km (n=4), >20km (n=2). Error bars are shown.

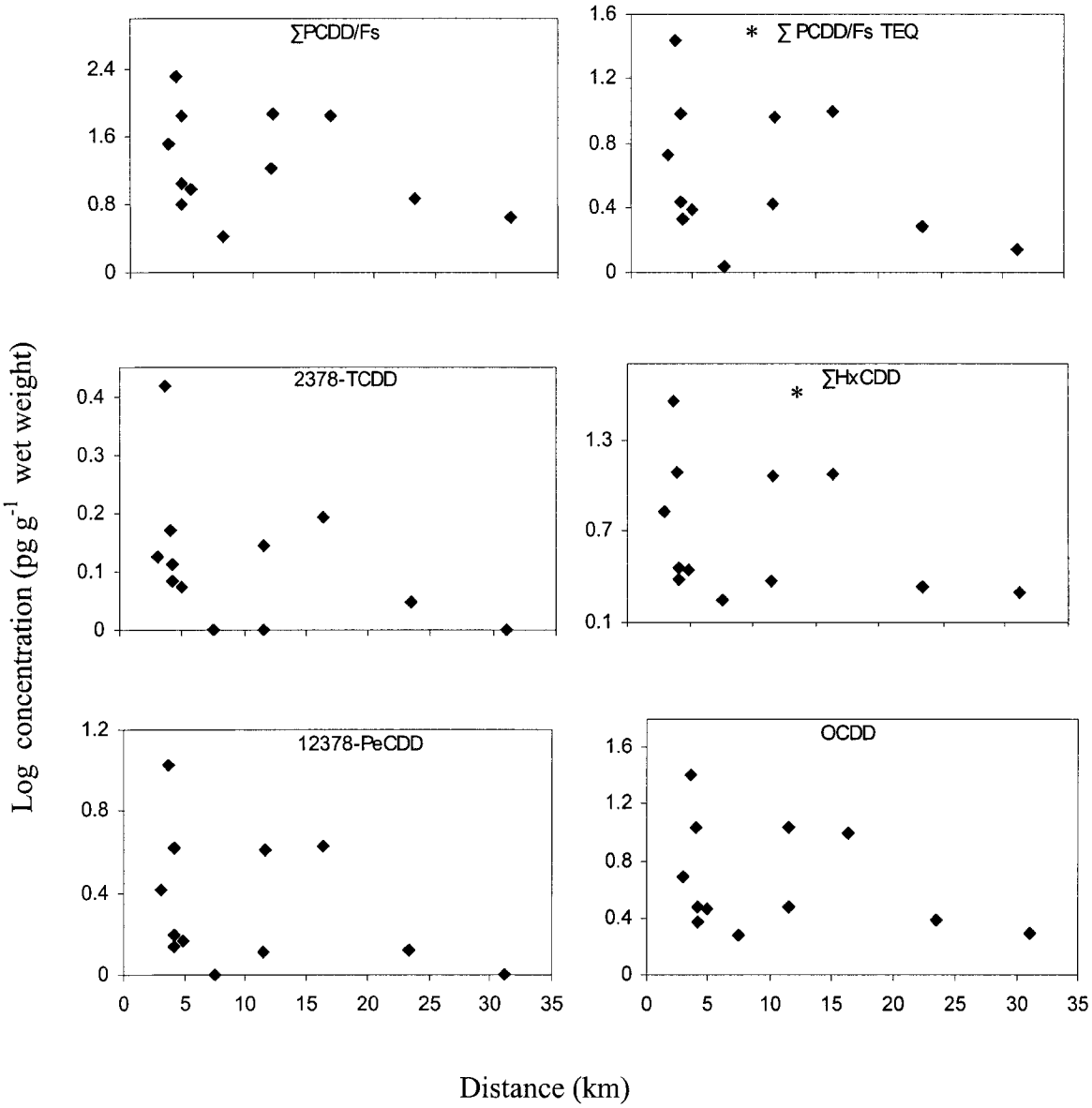


Figure 3.15 Relationship between concentrations of select PCDD/F congeners in deer and distance from the smelter.

Points represent log concentrations in deer fat at specified distance units (km) from the smelter and are expressed in pg/g wet weight (n=12).

* ∑PCDD/Fs expressed in pg TEQ g^{-1}

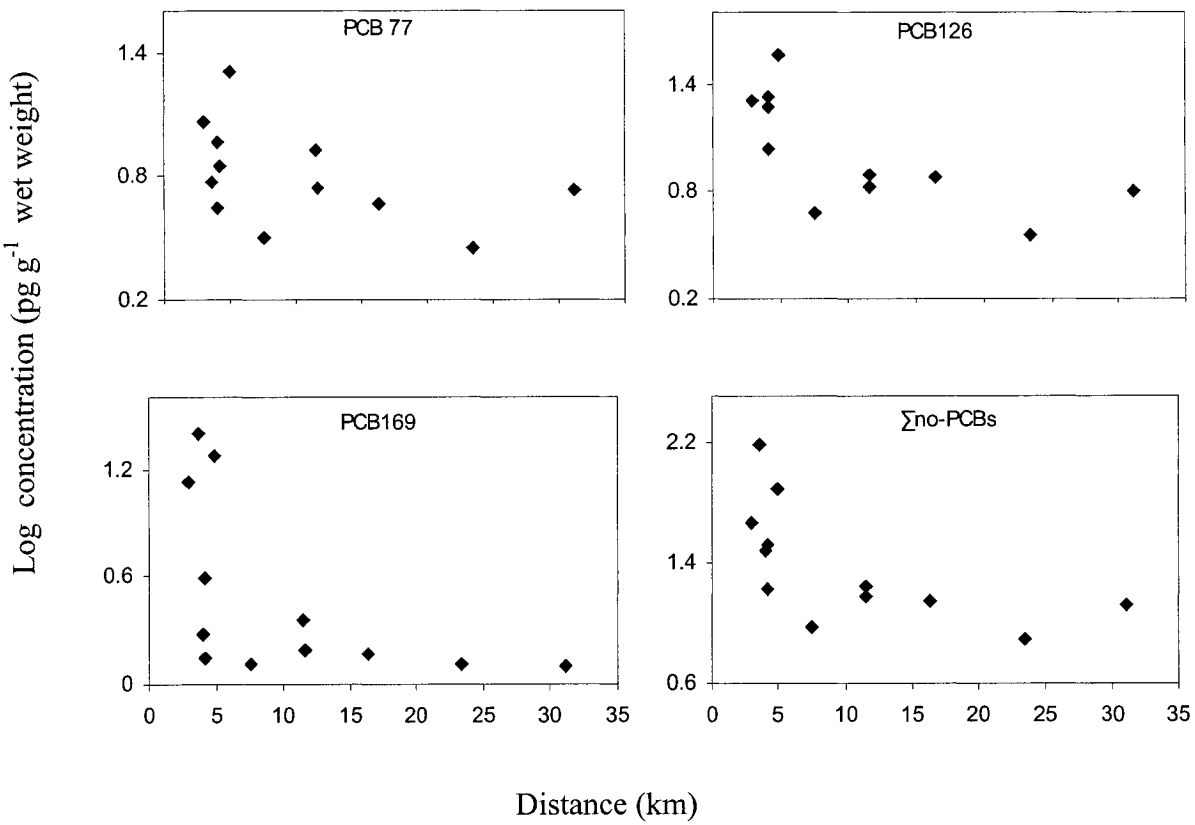


Figure 3.16 Relationship between concentrations of coplanar PCB congeners in deer and distance from the smelter.

Points represent log concentrations in deer fat at specified distance units (km) from the smelter and are expressed in pg g^{-1} wet weight (n=12).

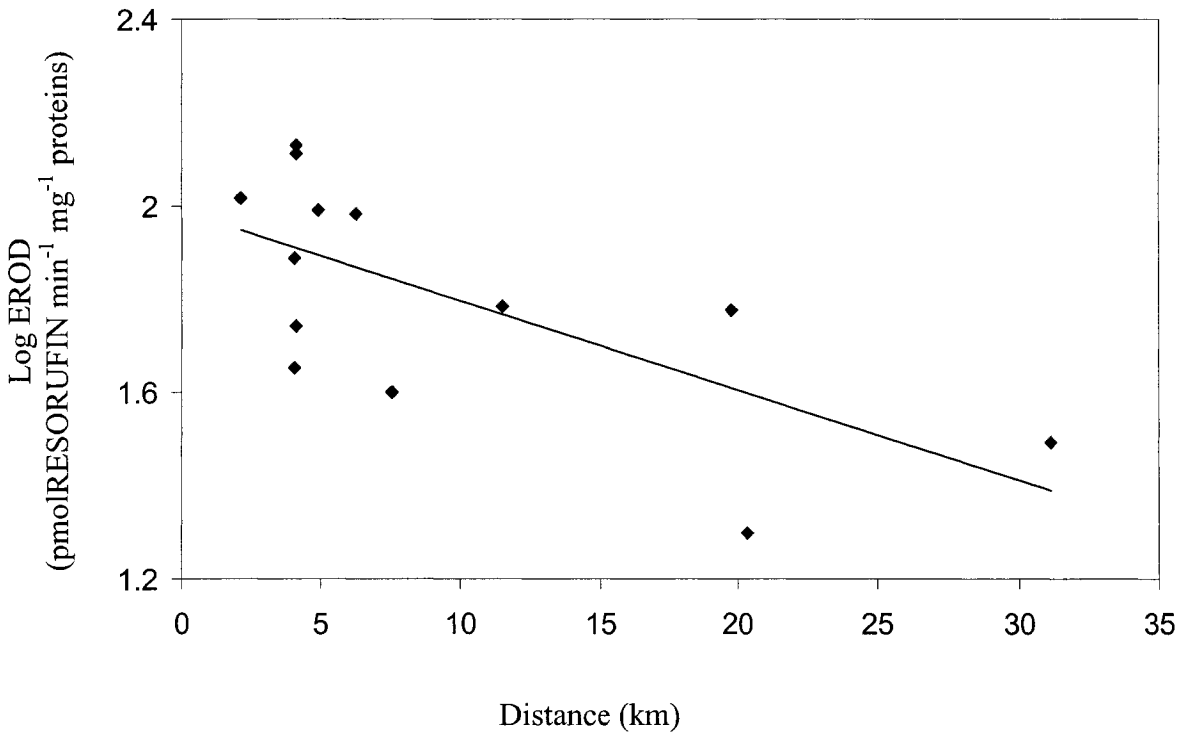


Figure 3.17 Ethoxyresorufin-*O*-deethylase activity (EROD) in deer and distance from the smelter.

EROD activity was measured in pmol RESORUFIN min^{-1} mg^{-1} proteins from 13 deer liver samples.

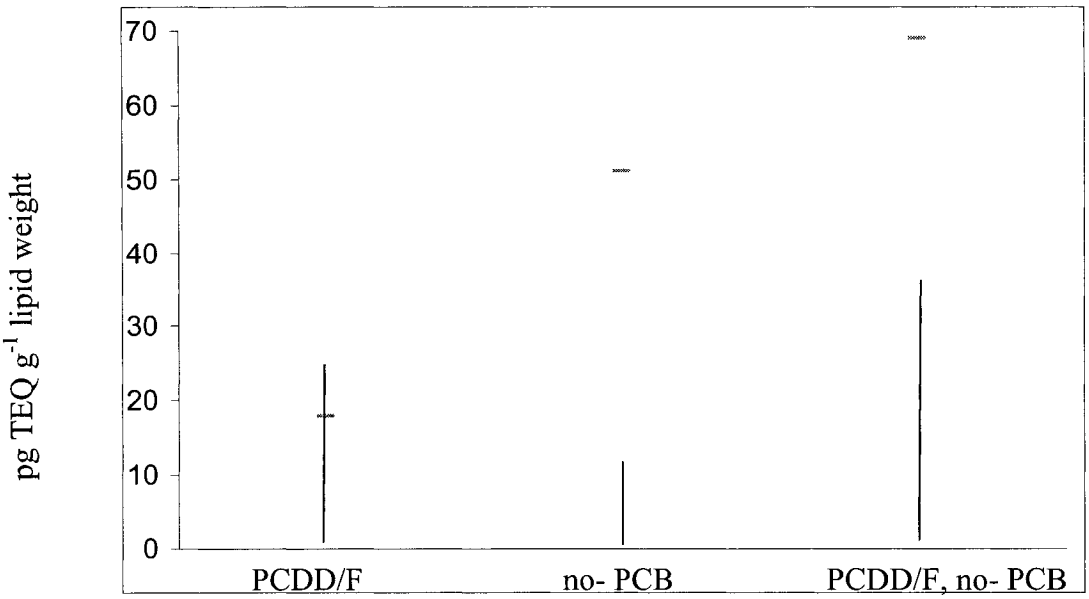


Figure 3.18 Levels of PCDD/Fs and coplanar PCBs (no-PCBs) in deer in this study measured against thresholds for immunosuppression in harbour seals.

Thresholds are indicated by red dashes (-), and ranges of the contaminant levels in deer (n=12) are indicated by vertical lines.

(de Wit el al. 2002)

4.0 Discussion

4.1 Polychlorinated Biphenyls and Hexachlorobenzene

The PCB levels in this study fell within the range of numbers reported from other studies of terrestrial herbivores in Europe and North America and HCB levels were for the most part lower (Table 3.1). The mean ∑PCB concentrations for the deer in 1999 (4.0±0.2ng/g lipid) were similar to low levels reported in wild reindeer in Finland (3.5ng/g lipid). The mean PCB concentrations in 2002 (6.2±0.8ng/g lipid) were lower than most of those reported in Europe and North America. However, the mean PCB concentrations of deer within 5km of the smelter (11±2.9ng/g lipid, n=10), and that of the most contaminated deer that was both within 5km of the smelter and in the prevailing wind direction (37±0.9ng/g lipid), were similar to values found in European deer muscle by Naso et al. (2004) (11.2ng/g lipid), and in caribou fat from the Canadian North found by Elkin and Bethke (1995) (16.5±5ng/g lipid), Thomas and Hamilton (1988) (38±13.7ng/g wet weight), and Muir et al. (1988[2]) (43ng/g ww). However concentrations reported in these ungulates were considered to be evidence of regional or long-range contamination, whereas levels in this study showed evidence of contamination from a point-source. There was variation in how "low" and high" levels were delegated in the different studies, for example, Falandysz and Kannan (1992) considered their reported mean ∑PCB concentration in fat tissue (32ng/g lipid) low in a region possibly contaminated from past pesticide use, as did Zasadowski et al. (2003) of their reported mean ∑PCB (4ng/g lipid). Variation in PCB concentrations can also be explained by the type of sample, as liver tends to accumulate much higher contaminant levels than fat, and muscle is even lower. None of the studies reported that the PCB and HCB levels were high enough to cause concern for human consumption, nor did they exceed thresholds for mammalian effects (de Wit et al. 2002).

Contrasts were seen in PCB concentrations in deer near (<5km) and far (>15km) from the smelter, particularly for the mid-range PCB homologues. Other studies have cited contrasts in contaminant levels near and far from a point-source; for example, Gabos et al. (1998) found ∑PCBs in muscle significantly elevated in deer within 20km of a point source compared to those beyond 20km. Another study concluded that caribou were accumulating PCBs from an abandoned radar site in Sagelek Bay by citing contrasts in ∑PCB in caribou fat from the site (68-365ng/g lipid) and those 6km away (7.8-13ng/g lipid) (Gregor et al. 2003).

The mid-range PCB homologues, like hexachlorobiphenyl, pentachlorobiphenyl, and heptachlorobiphenyl, were detected in the greatest proportions in the deer (31.7%, 18.7%, and 16.7%, respectively) relative to the lighter and heavier PCBs. This was consistent with other studies of PCB accumulation in deer and caribou (Thomas et al. 1992)(Figure 4.1). Two of the studies examined PCBs in caribou fat as a result of long-range transport (Thomas and Hamilton 1998, Muir et al. 1988[2]) and the study by Gabos et al. (1998) looked at deer muscle contaminated from a point-source. Deca- and nona- chlorobiphenyls were consistently present in low proportions, although deca- was not measured in the former two studies and was not shown (Figure 4.1). In this study, concentrations of the pentachlorobiphenyl, hexachlorobiphenyl, heptachlorobiphenyl and octachlorobiphenyl homologue groups also showed significant inverse relationships with distance from the smelter (Figure 3.6). These compounds bioaccumulate in the food chain because they are not easily metabolized, have high $\log K_{ow's}$ and have relatively high bioconcentration factors (5.3-6.2) (Table 1.3, Figure 1.3). The low-range PCBs did not show any trends with distance from the smelter and a large proportion were not detected, such as mono+dichlorbiphenyls, where a small proportion of the samples (14%) were above detection limits (Appendix 3.3).

This is unlike studies documenting greater concentrations of lower-chlorinated PCBs in terrestrial herbivores relative to mammals at higher trophic levels as a result of long-range contamination (Muir et al. 1988[1], Larsson et al. 1990, Elkin 1994). However these PCBs have lower $\log K_{ow's}$ and BCFs, so they are more readily metabolized and less likely to bioaccumulate.

The homologue pattern measured in the deer did not follow that measured from the smelter stack emissions (Figure 4.2, Appendix 1.1). The inconsistency can be explained by differential homologue transformation, as PCB levels change upon emission as they partition and degrade in the environment and are concentrated to varying degrees in biota. The relative abundance of decachlorobipenyl was greatest in the stack emissions (65%), while it comprised less than 1% in deer. Despite the high $\log K_{ow}$ of this homologue, its estimated BCF (4.02) is lower than that of the mid-range PCB homologues (5.0-6.2), and is similar to the BCF values reported for the low-range PCBs (3.4-4.2) which likewise did not bioaccumulate strongly in the deer (Table 4.1). In addition, Geyer et al. (1987) estimated very low BCF values for decachlorobiphenyl in humans (1.32-1.48). In general the absence of the most highly-chlorinated PCBs in the deer, such as the nona- and deca-CBs, reflects a typical PCB bioaccumulation pattern, where BCF decreases with an increasing $\log K_{ow}$ because the large molecular size of these congeners impedes their particle diffusion through cellular membranes (Figure 1.3, Table 1.3) (Connell and Hawker 1988, Newman and Unger 2003).

The lack of relationship between PCB concentrations and age of the deer was consistent with a study by Naso et al. (2004) that found no differences in PCB concentrations between juvenile and adult deer in a contaminated area. In this study the sample collection did not encompass a wide range of ages and it was impossible to ensure that the samples had

an equal representation in each cardinal direction (north, south, east, west). There was only one sample in 2002 that lay within both the prevailing wind direction and within 5km of the smelter. Although this sample had the greatest concentration of PCBs (35ng/g), the number of samples in this area did not comprise a large enough grouping to yield statistically significant results for prevailing wind direction as an explanatory variable.

Significant differences between the 1999 and 2002 concentrations were detected in the only organochlorine pesticide emission product from the smelter, HCB. Many of the non-emission products from the smelter were not detected at all (Appendix 3.4) and those that were did not show trends with space and time, such as a-endosulfan (Figure 3.8). Like the lower-chlorinated PCBs, HCB is very volatile (Table 1.3) and a significant inverse relationship with distance was not found in 2002. These results are consistent with a study by Gregor et al. (2003) that found great contrasts in $\sum$PCB levels in caribou near and far from an abandoned radar site but did not find significant differences in the organochlorine pesticides. Blais et al (2003) found an inverse relationship with PCBs in vegetation and distance of a hazardous waste smelter, but HCB did not show a decline with distance. Among the 24 non-emission products, Dieldrin was detected in approximately 75% of the samples and showed a significant decline with distance from the smelter. The one compound this is within the allowable margin of error as specified by the 95% confidence interval (Zar 1999). Both aldrin and dieldrin have been banned as soil insecticides, and in Canada existing stocks were sold, used, or disposed of by 1995 (NPRI, 1996). However dieldrin is very persistent, with a half life in soil of over 7 years, and its high $\log K_{ow}$ (6.2) and non-polar nature render it bioaccumulative (Mackay 1992c, de March et al. 1998). Traces of dieldrin also result from aldrin, as the former is rapidly metabolized from aldrin in plants and animals, and rats have been shown to metabolize large doses of aldrin into dieldrin in as little

as 2 hours (Van Esch, G.J. 1989). Due to long range atmospheric transport, dieldrin has been detected in regions where it was never produced, such as the arctic, and other sources today may also be a result of stocks of the chemical used for underground termite control (NPRI 1996, de March et al. 1998).

4.2 Polychlorinated Dibenzo-Para- Dioxins and Dibenzofurans

The average of the sum of ∑PCDD/Fs and ∑no-PCBs in this study were 5.28pgTEQ/g and 2.28pgTEQ/g respectively, and the sample located in the prevailing wind direction and in close-range to the smelter had the highest concentrations of ∑PCDD/Fs (26.46pgTEQ/g) and ∑no-PCBs (12.33pgTEQ/g). These concentrations were close to those measured in deer muscle (32pg/g TEQ, n=3) by Gabos et al. (1998) within a 20km radius of an accidental PCB and PCDD/F spill from a waste treatment plant. ∑PCDD/Fs and ∑no-PCBs measured 5 years after the spill in deer (fat) up to 30km from the source (5.6pgTEQ/g and 2.47pgTEQ/g respectively, n=7) were very similar to the average concentrations reported in this study (MacKenzie et al. 2005). The ∑PCDD/F levels found in the hotspot deer in this study were also similar to concentrations in reindeer from the Russia's Kola Peninsula (20pgTEQ/g), an intensively mined region known to be one of the most polluted in the arctic (RAIPON/AMAP/GEF 2001). Other studies reported contaminant levels lower than those found in this study, for example, Hebert et al. (1996) measured combined levels of PCDD/Fs, no-PCBs and mono-*ortho* PCBs in caribou from the Canadian North (0.3-3.3pgTEQ/g lipid weight), and de Wit et al. 1994 reported a range of 0.9-1.93pgTEQ/g lipid weight in reindeer in Sweden.

The contaminant concentrations found in this study were measured against thresholds for immunosuppression in harbour seals, and only the ∑PCDD/F concentrations in the deer located in the prevailing wind direction and in close-range to the smelter (35.14 pgTEQ/g)

exceed the threshold (18pgTEQ/g) (Figure 3.18), as did the ∑PCDD/F levels in deer reported by Gabos et al. (1998), and in reindeer from Russia by RAIPON/AMAP/GEF (2001). However, there may be differences in susceptibilities to PCDD/Fs between species and further testing needs to be conducted on deer themselves, and on ungulates more similar to deer (such as bovine) in order to accurately extrapolate immunosuppression data thresholds to deer.

The coplanar ∑PCBs showed a significant decline with distance; PCB-126 showed the strongest relationship, PCB-77 showed the weakest (Figure 3.16). PCB-77 is a tetrachlorobiphenyl and is more volatile and has a lower $\log K_{ow}$ than PCB-126 (pentachlorobiphenyl) and PCB-169 (hexachlorobipehnyl), hence it does not bioaccumulate in fatty tissue as much. PCB-126 was present in the greatest proportions (97%), and this has been reported in other studies. For example, Muir et al. (1996) showed a prevalence of PCB-126 among coplanar PCBs in arctic beluga blubber (wet weight), and Gabos et al. (1998) found PCB-126 accounted for 86% of the total coplanar PCB (TEQ) concentration in deer. The most toxic PCDD/F congener 2,3,7,8-TCDD with a TEF of 1 demonstrated the most significant decline with distance ($p<0.1$) relative to the other congeners (Table 3.5). Other studies have documented general trends showing declines in ∑PCDD/Fs with distance from a source in soil samples (n=38-47) and in deer (n=3) (Gabos et al. 1998, Lorber et al 1998, Sandalls et al. 1998, Park et al. 2004).

Overall the congener patterns in deer did not resemble those of the stack emissions. There is disagreement about whether congener patterns may be related to those of emissions sources (Sandals et al. 1998). Lorber et al. (1998) conducted an impact study characterizing the environment near an incinerator known to be a great source of PCDD/Fs. Although evidence of the point source was clear, for example, a decline in soil concentrations with

distance, PCDD/F signatures in soil at close range (within 1km) to a waste incinerator and in the prevailing wind direction did not closely resemble the stack pattern. It was concluded that identifying a point-source with the sole use of PCDD/F congener patterns is unreliable due to chemical transformations between emission, deposition, and further modification in the environment.

One of the ways that the differences between the PCDD/F congener distributions reported in smelter emissions and those found in the deer can be accounted for is through a bioconcentration factor (BCF). BCF values were adopted from those used by Lorber et al. (1994) in the validation of a model designed to predict PCDD/F concentrations in beef from independent air emission datasets (Lorber, US EPA, personal communication, McLachlan, Univeristy of Bayreuth, personal communication). The latter study itself used BCF values developed by MacLachlan et al. (1990) for milk fat, which provided the only dataset where BCFs were estimated for 98% of the PCDD/F congeners. Cattle were the most similar species to deer with such data available, and in the UK anti-parasitic drugs tested for cattle have been used for deer based on similarities in contaminant metabolism (Sivapathasundaram et al. 2003). 1,2,3,7,8 PeCDD showed the greatest difference in abundance between the smelter emissions and deer, with relative abundances measured at 5% and 36%, respectively, and this congener coincided with a high BCF value (4.16). 2,3,7,8-TCDD and the Hx-CDDs also had high BCF's (4.32 and approximately 2, respectively) which were consistent with the greater relative abundances reported in the deer compared to the smelter emissions (Table 3.4). 2,3,7,8-TCDF and 1,2,3,7,8-PeCDF were present in greater abundances in the smelter emissions (12% and 8.7% respectively) than in the deer (1.8% and 1.5% respectively) and these had low BCF values of 0.94 and 0.73, respectively (Table 3.4). 2,3,4,7,8-PeCDF was present in large proportions in the smelter

emissions as well as in the deer (20 and 22% respectively), and this coincided with a large BCF of 3.1.

The ratio of the relative abundance of PCDD/F congeners in deer relative to air showed a positive significant linear relationship with the BCF values, indicating that the congeners which concentrated in the deer in this study coincided with the high BCF values reported by Lorber et al (1994), while the congeners that had high abundances in the air but did not concentrate in the deer coincided with low BCF values (Figure 3.11). Additionally, the relationship between relative abundance of PCDD/F congeners in air and BCF values did not show a significant positive relationship (Figure 3.11). This indicates that bioconcentration can account for differences in congener patterns in the smelter emissions and the deer, supporting the previous results indicating that the smelter is the principal point-source of PCDD/Fs.

Differences in PCDD/F congener profiles in the deer and smelter emissions can also be caused for by their transformation and degradation as they partition from the air into environmental media. The more highly chlorinated PCDD/Fs are less volatile and favour particulate-bound phases in the atmosphere, which are scavenged into environmental sinks more efficiently than the lower-chlorinated PCDD/Fs (ATSDR 1998). These are more volatile and exist to a greater extent in the vapour phase, where they remain in the atmosphere for longer periods of time and are subject to photodegradation through gas-phase reactions with hydroxyl radicals (OH) present in the atmosphere from the degradation of ozone and hydrogen peroxide (Brubaker and Hites 1997, ATSDR 1998, Baker and Hites 2000).

Czuczwa and Hites (1986) and Hites (1990) measured a predominance of the highly chlorinated PCDD/F congeners in lake sediments, in particular OCDD, and Baker and Hites

(2000) showed the loss of lower-chlorinated PCDD/Fs from air to sinks in the environment in a figure contrasting PCDD/Fs measured from incinerator sources in the US and soil sink profiles (Figure 4.3). These trends reflect contrasting PCDD/F profiles in emissions and deer seen in this study (Figure 3.10). However, global mass balance studies have found that PCDD/F deposition (in particular OCDD) far exceeds emissions, pointing to the possibility of non-anthropogenic sources (Czuczwa and Hites 1986, Baker and Hites 2000, Park et al. 2004). The atmospheric conversion of aqueous PCP (pentachlorophenol), a wood preservative, is a major source of OCDD, and this is being investigated further (Czuczwa and Hites 1986, Baker and Hites 2000, Park et al. 2004).

4.3 Ethoxyresorufin-*O*-deethylase Activity

In this study a significant relationship was found between distance and EROD activity in the deer liver, mirroring the trend that was seen with PCBs (Figure 3.5, 3.17). The relationship between EROD activity and total PCBs in deer fat was close to significance ($p=0.053$, $n=14$). Similarly, Kuzyk et al. (2003) found an inverse relationship between distance and total PCBs in black guillemot livers and reported a significant positive linear relationship between EROD activity in the liver and total PCBs in the liver, with a larger sample size ($n=33$) than used in this study ($n=14$). Some literature validates the use of EROD as a biomarker of exposure by showing, in addition to induction, a positive significant relationship between EROD activity and the PCB body burden. However, this literature primarily focuses on the PCB concentrations in *liver* tissue, whereas deer fat was analyzed in this study (Letcher et al. 1996, Jørgensen et al. 1999). Many studies use EROD induction as evidence of contamination without showing a positive relationship between EROD activity and contaminant body burden. For example, Nyman et al. (2000) found that EROD activity was up to five times greater is seals from polluted versus non-polluted waters. Siroka et al.

(2005) used EROD induction as evidence of contamination in fish from heavily polluted waters, but was unable to positively correlate this with PCB concentrations in fish tissue and sediment, and it was thought that this was due to an acquired resistance to EROD induction because of chronic contaminant exposure (Brammell et al. 2004). Deviations from this positive relationship between EROD activity and the PCB body burden have also been reported, for example, Henriksen et al. (1998) found a negative relationship between EROD activity and PCB body burden in glaucous gulls that were fed PCB contaminated fish, and authors indicated this was likely due to the reduced metabolic capacity in this species for these particular contaminants.

The mean ethoxyresorufin *O*-deethylase (EROD) activity measured in this study was 71.72±9.5pmol min^{-1} mg^{-1} protein (n=14), encompassing values ranging from 19.9 - 134pmol min^{-1} mg^{-1} protein. This was similar to mean levels of EROD activity (66.52±6.36pmol min^{-1} mg^{-1} protein, n=5) in red deer from a non-industrialised UK park as reported by Sivapathasundaram et al. (2003) in the first study to document the expression of Cytochrome P450 families in deer liver. In this line of research, Cytochrome P450 composition was being characterized in both cattle and deer to evaluate the safety of treating deer with the same drugs licensed for cattle, an important issue for human consumers of venison. EROD activity has been successfully used as a contaminant biomarker in various other species and there is great variability among them. Metabolism rates of cytochrome P450 ethoxyresorufin *O*-deethylase substrates reported in cattle (n=5; 328±28 pmol min^{-1} mg^{-1} protein), herring gulls (10-180 pmol min^{-1} mg^{-1} protein), and mammals in the Canadian Arctic such as beluga whales (n=8; 413±263 pmol min^{-1} mg^{-1} protein) and polar bears (n=16; 518-1928 pmol min^{-1} mg^{-1} protein) show a wide range of values (White et al. 1994, Letcher et al. 1996, Sivapathasundaram et al. 2001, Kennedy et al. 2003). Variability of EROD

activity has also been reported within the same species, for example Goksoyr et al. (1992) reported differences between EROD activity between adult male hooded seals (30±7 pmol min^{-1} mg^{-1} protein) and adult male harp seals (2.1±1.4 pmol min^{-1} mg^{-1} protein) and also in the pups of the latter seal species (7.1±1.4 pmol min^{-1} mg^{-1} protein). Interspecies and interindividual variation are primarily due to differences in toxicokinetics, diet and nutritional status, hormonal factors, and polymorphisms in the CYP1A1 genes (Jørgensen et al. 1999, de Wit et al. 2002, Kennedy et al. 2003, Elskus et al. 2004, van Duursen et al. 2005). In addition, each study varies in that a number of other factors can affect EROD activity, such as exposure to other AHR agonists, and acquired resistance to toxicants (Brammell et al. 2004).

4.4 Human Health Risk Assessment

The quantity of PCDD/Fs and coplanar PCBs found in a single weekly portion of deer meat declined with distance from the smelter, and the number of portions that could be safely consumed in deer beyond 20km of the smelter were less restrictive than for those deer located within 5km, and also in the prevailing wind direction (Table 3.6). In this study, the sum of PCDD/F and coplanar PCBs found in a single weekly portion of deer meat with the maximum value of contaminants (from the region within 5km and in the prevailing wind direction) was 2.36 pg TEQ kg^{-1} bw $week^{-1}$, and it would require three 227g portions per week to exceed the lower end of the WHO TDI range (1 pg TEQ kg^{-1} bw day^{-1}or 7 pg TEQ kg^{-1} bw $week^{-1}$), and 11 portions per week to exceed the upper end of the range (4 pg TEQ kg^{-1} bw day^{-1} or 28 pg TEQ kg^{-1} bw $week^{-1}$). The Health Canada guideline, which lies approximately in the middle of the WHO range (2.5 pg TEQ kg^{-1} bw day^{-1}) allows for no more than 30 meals per month (extrapolated to 7.5 per week) of the deer located within 5km of the smelter and in the prevailing wind direction (maximum value deer), and an

unrestricted number of meals in deer beyond 20km of the smelter. For children and toddlers, the intake limits were more restrictive because their intake versus bodyweight is the highest of all human age groups (Health Canada 1994). Consuming more than one and a half and two portions per week of the maximum value deer located within 5km and also in the prevailing wind direction, and more than five and seven portions per week of deer within 5km of the smelter in all cardinal directions (N,S,E,W), exceeds the lower-bound range of WHO's TDI for toddlers and children, respectively (Table 3.7). Health Canada guidelines are exceeded if more than 3.5 and 5 portions per week of the maximum value deer are consumed for toddlers and children, respectively, and the limits lie beyond realistic consumption for deer in other location groupings.

The WHO tolerable daily intake (TDI) for coplanar PCBs and dioxins and furans, 1-4 pg TEQ kg^{-1} bw day^{-1}, stipulates that "the upper range of 4 pg TEQ kg^{-1} bw day^{-1} is considered the maximal TDI on a temporary basis and the ultimate goal is to reduce human intake levels below 1pg TEQ kg^{-1} bw day^{-1}" (WHO 2000). The evaluation of safe consumption in this study applies the various levels of deer contamination to the entire WHO range. A conservative approach was used by Easton et al. (2002) by applying the lower-bound value in the WHO's TDI range (1pg TEQ kg^{-1} bw day^{-1}) to evaluate the safety of contaminated farmed salmon consumption, recommending that people limit their intake so that it would fall below the latter value. Other studies have interpreted the TDI using a cost-benefit type of approach, weighing the risks of exceeding it versus nutritive benefits of the foodstuffs. In some cases where contaminant levels in food has exceeded the TDI, such as farmed salmon (PCDD/Fs) and traditional foods in the Canadian North (PCBs), continued consumption has been recommended because it is thought that the nutritive and cultural benefits outweigh the risks of contamination (Kinloch et al 1992, Stoksad 2004).

The calculated number of portions was determined for uncooked meat, and employing various cooking treatments may reduce the total concentration of some contaminants. A study by Salama et al. (1998) reported reduction of PCB levels with the cooking of bluefish fillets. While PCB levels from raw to cooked fish did not change with convection oven baking and pan frying, PCB losses of 65%, 60%, 46%, and 37% were reported with smoking, microwave, charbroiling (skin off), and charbroiling (skin on), respectively. However, the degree to which cooking reduces contaminant levels may vary across different species, as well as between PCBs (solely tested by Salama et al. 1998) and PCDD/Fs, the latter of which was the focus of consumption recommendations made in this study. Removal of fat from the venison meal may also reduce contaminant concentrations, as fat contains higher concentrations of contaminants than the muscle, which has a very low fat content (1.87%).

In many industrialized countries, the average daily intake of PCDD/Fs and coplanar PCBs from foodstuffs exceeds the lower-bound value of the TDI (1pg TEQ kg^{-1} bw day^{-1}). This was the case in Quebec, where the background dose of PCDD/Fs in commonly consumed fatty foods in the province is 7.25 pg TEQ kg^{-1} bw $week^{-1}$ or 1.035 pg TEQ kg^{-1} bw day^{-1} (Health Canada 1993[2]). Intake of PCDD/Fs and coplanar PCBs from foodstuffs mainly of animal origin (meat, cheese, milk) in Spain were reported at 3.22 pgTEQ kg^{-1} bw day^{-1} and a similar survey in Belgium reported 2.04 pg TEQ kg^{-1} bw day^{-1}. These studies concluded that these levels were safe because they were *within* the WHO range of 1-4 pg TEQ kg^{-1} bw day^{-1}, but the studies also stipulated the need to reduce PCB and dioxin and furan emissions to lessen the contamination of foodstuffs (Focant et al. 2002, Fernandez et al. 2004).

4.5 Conclusions

An impact of the Magnola smelter was seen in the elevated levels of PCBs in deer which were sampled while the smelter was operational in 2002, compared to those from 1999, a year before the smelter opened. In addition, a significant inverse relationship with distance from the smelter was detected in the 2002 deer only (Figure 3.5). Using the "BACI" (before-after control-impact) design, which involved grouping the data into deer "near" and "far" from the smelter, results showed elevated PCBs in 2002 in close proximity (<5km) to the smelter (Figure 3.3). The trends described above were detected only in the mid-range PCBs (Figure 3.6). These particular homologues are typically detected in biota, a pattern that corroborates the behavior of different PCBs due to their range of chemical properties, namely lipophilicity, volatility and molecular size, as exemplified in a model by Connell and Hawker (1988) (Figure 1.3) (Muir et al. 1988[2], Thomas and Hamilton 1988, Gabos et al. 1998). An additional analysis conducted in an Environment Canada laboratory of coplanar PCBs, which are the most toxic of all PCBs due to their dioxin-like configuration and effects, also showed a significant decline with distance in 2002 (Figure 3.16). A commonly used biomarker of contaminant exposure, induction of the cytochrome P450 liver enzymes, was detected in the deer in an EROD assay, and also displayed a significant inverse relationship with distance from the smelter (Figure 3.17). EROD activity was measured in deer for the first time in a study by Sivapathasundaram et al (2003), and the mean EROD activity reported was similar to that measured in this study. Significant differences between 1999 and 2002 were detected in the organochlorine pesticide HCB, an emission product, and this was not found for non-emission products, for example, a-endosulfan (Figure 3.8).

Differences in the congener profiles in the deer and smelter emissions can be explained by their transformation and degradation as they partition from the air into

environmental media. The ratio of the relative abundance of PCDD/F congeners in deer relative to air showed a positive significant relationship with bioconcentration factors (BCFs), indicating that the congeners which concentrated in deer in this study were those with high BCF values (Figure 3.11) (Maclachlan et al. 1990, Lorber et al. 1994, Lorber et al. 1998, Sandalls et al. 1998). A high abundance of decachlorobiphenyl and a low proportion the other PCB homologues (<10%) were measured in the stack emissions, and this pattern was not reflected in the deer (Figure 4.2). This reflects a typical PCB bioaccumulation pattern described in a model by Connell and Hawker (1998), where BCF's decrease with increasing lipophilicity ($\log K_{ow}$) only for the most highly chlorinated PCBs because their large molecular size impedes their accumulation in tissues (Figure 1.3, Table 1.3) (Newman and Unger 2003).

The risk of adverse health effects posed to humans by local deer was analyzed by applying contaminant concentrations in the deer to consumption guidelines. The World Health Organization (WHO) specifies a tolerable daily intake (TDI) range for coplanar PCBs and PCDD/Fs of 1-4 pg TEQ kg^{-1} bw day^{-1} (WHO 2000), and Health Canada has temporarily adopted a tolerable monthly intake (PTMI) of 70 pg kg^{-1} bw $month^{-1}$, which lies approximately in the middle of the WHO range at 2.5 pg TEQ kg^{-1} bw day^{-1}. In general the number of portions required to exceed safe levels increased with the distance from the smelter. Intake levels were most restrictive for a sample located within 5km of the smelter and in the prevailing wind direction (NE), as it would require 3 portions per week to exceed the lower end of the WHO TDI range (1 pg TEQ kg^{-1} bw day^{-1}or 7 pg TEQ kg^{-1} bw $week^{-1}$), 11 portions per week to exceed the upper end of the range (4 pg TEQ kg^{-1} bw day^{-1} or 28 pg TEQ kg^{-1} bw $week^{-1}$), and no more than 30 meals per month (extrapolated to 7.5 per week) according to the Health Canada guideline (Table 3.6). With the same criteria applied to

toddlers and children, intake was more restricted, requiring 1.5 portions per week to exceed the lower end of the WHO TDI range and 6 portions per week to exceed the upper end of the range for toddlers, and 2 to 8 portions per week for children (Table 3.7). This contrasts with an unrestricted number of meals of deer located beyond 20km of the smelter.

The WHO tolerable daily intake (TDI) for coplanar PCBs and dioxins and furans stipulates that "the upper range of 4 pg TEQ kg^{-1} bw day^{-1} is considered the maximal TDI on a temporary basis and the ultimate goal is to reduce human intake levels below 1pg TEQ kg^{-1} bw day^{-1}" (WHO 2000). This range leaves room for interpretation and it has been applied on a case-by case basis. For example, a conservative approach was used by Easton et al. (2002) in the evaluation of farmed salmon consumption, and the study concluded that people were at risk of adverse health effects by exceeding the lower-bound value in the WHO's TDI range. In contrast, traditional foods in the Canadian North exceed the TDI, however continued consumption has been recommended because the nutritive and cultural benefits outweigh the risks of contamination (Kinloch et al 1992, Stoksad 2004). In addition, average daily intake of PCDD/Fs and coplanar PCBs from foodstuffs exceeds the lower-bound value of the TDI in many industrialised countries, and this was also the case in Quebec (Health Canada 1993[2]). Studies have concluded that levels within the WHO range of 1-4 pg TEQ kg^{-1} bw day^{-1} are safe, but they also stipulated the need to reduce PCB and dioxin and furan emissions to lessen risk of consuming foodstuffs (Focant et al. 2002, Fernandez et al. 2004). Due to the wide range of interpretations of the TDI range, this study reports results using WHO's entire range, and also Health Canada's temporary guideline.

In order to reduce contaminant concentrations, removal of fat from the venison is recommended, as fat contains higher concentrations of contaminants than the muscle, which has a very low fat content (1.87%). Also certain methods of cooking (smoking, microwave,

charbroiling) have been reported to reduce PCB levels in fish fillets (Salama et al. 1998). However, the degree to which cooking reduces contaminant levels may vary across different species, as well as between PCBs and PCDD/Fs, the latter of which was the focus of consumption recommendations made in this study.

A standard commonly used to evaluate the health risks posed to terrestrial mammals is a threshold value for immunosuppression in harbour seals (Ross et al. 1995, de Wit et al. 2002). Applied to the deer in this study, dioxin and furan levels of the most contaminated deer near the smelter exceeded this threshold.

The results of this study must be considered within the context of the smelter's activities. Magnola was operational between the years 2000-2002, at which time it took a temporary hiatus, reportedly due to the rise in cheaper magnesium exports from China. During operations, it was producing at only 16% and 43% of its full capacity in 2001 and 2002 respectively, and it was Canada's fifth largest source of dioxins and furans in 2002 (Table 1.2) (Environment Canada 2004, Environmental Defence and CELA 2004). The impact of the smelter detected in this limited time is to be considered for possible future operations of the smelter and for similar industrial processes. Additionally, it would be advisable to conduct a post-impact assessment because the chemicals released persist in the environment for long periods of time, and they may have an impact on the environment long after their release (Table 1.3).

Table 4.1 Bioconcentration factors (BCF) for PCB homologues.

Values are estimated from fish (sources a-c) and humans (d). References: (a) Mackay et al. (1992a); (b) Mackay et al. (1989); (c) Gobas et al. (1987); (d) Geyer et al. (1987).

PCB Homologue	BCF	Reference
Monochlorobiphenyl	3.4	a
Dichlorobiphenyl	3.8	a
Trichlorobiphenyl	4.2	a
Tetrachlorobiphenyl	4.6	a
Pentachlorobiphenyl	5.0-5.3	a,b
Hexachlorobiphenyl	5.39	a
Heptachlorobiphenyl	5.8	a
Octachlorobiphenyl	6.2	a
Nonachlorobiphenyl	6.6	a
Decachlorobiphenyl	4.02	c
	1.32-1.48	d

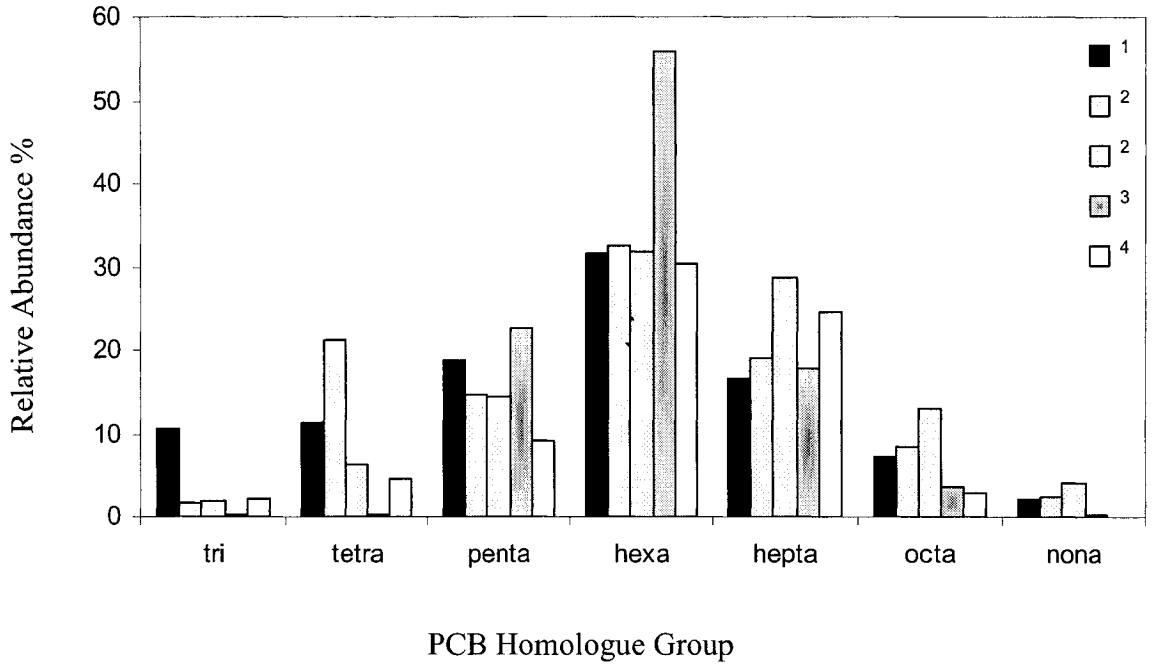


Figure 4.1 Mean composition of PCB homologue groups in samples from deer in the Danville region compared to levels in caribou and deer from other studies.

Mean composition is expressed as a % of total PCBs. [1]Deer fat in the Danville region, present study (n=43); [2]Thomas and Hamilton 1988 (caribou fat reported separately in two NWT regions); [3] Muir et al. 1988[2] (caribou fat from NWT); [4]Gabos et al (1998) (deer muscle from a point-source, n=3).

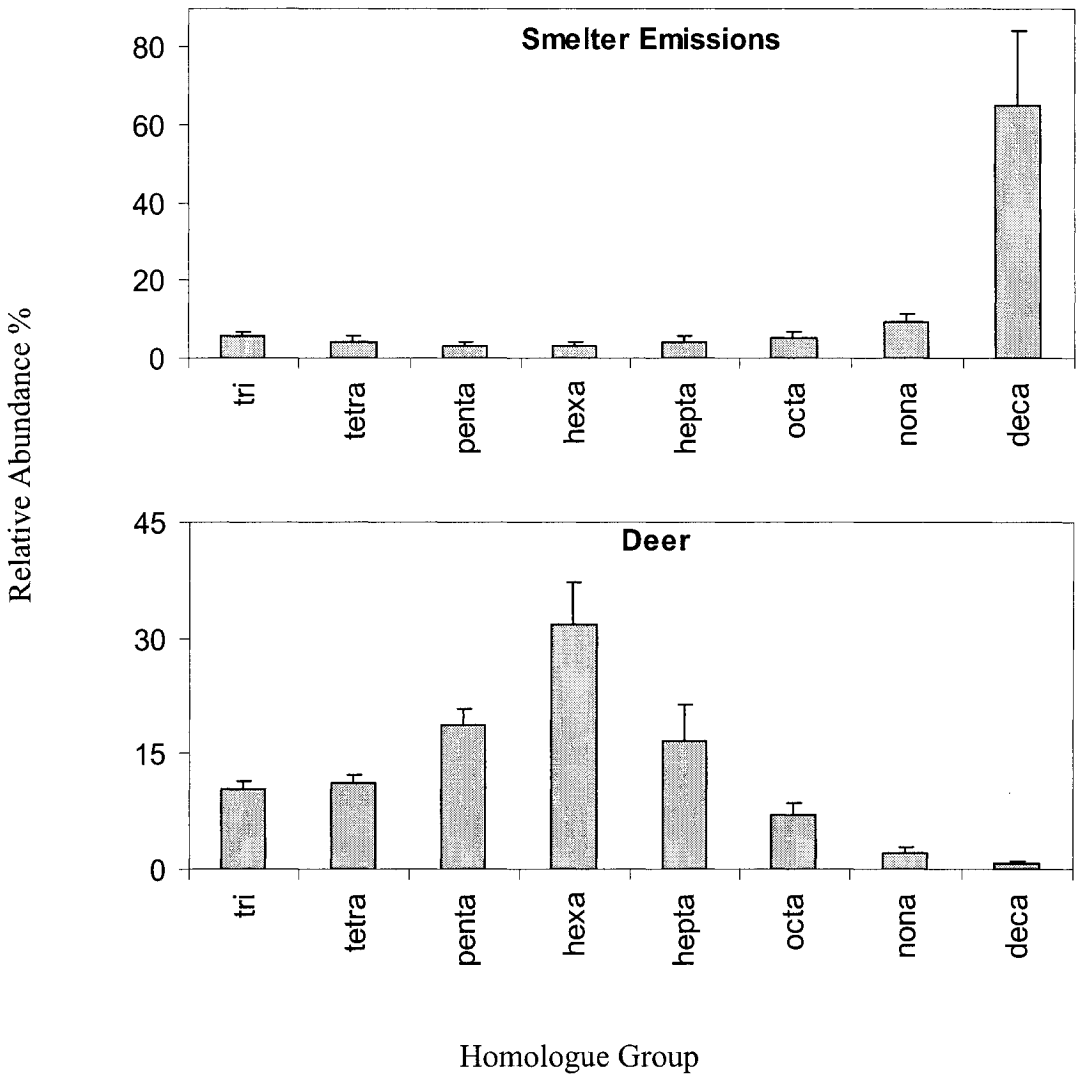


Figure 4.2 Relative abundance of PCB homologues in smelter emissions compared to deer.

Relative abundances are expressed as a % of total PCBs and standard errors are shown. The smelter emissions are a mean of 6 tests conducted by The Quebec Ministry of the Environment (MENV) from August to December 2002 reporting releases (ng) from the electrolysis chambers (Appendix 1.1). PCBs in the 2002 deer (n=43) were measured in ng/g.

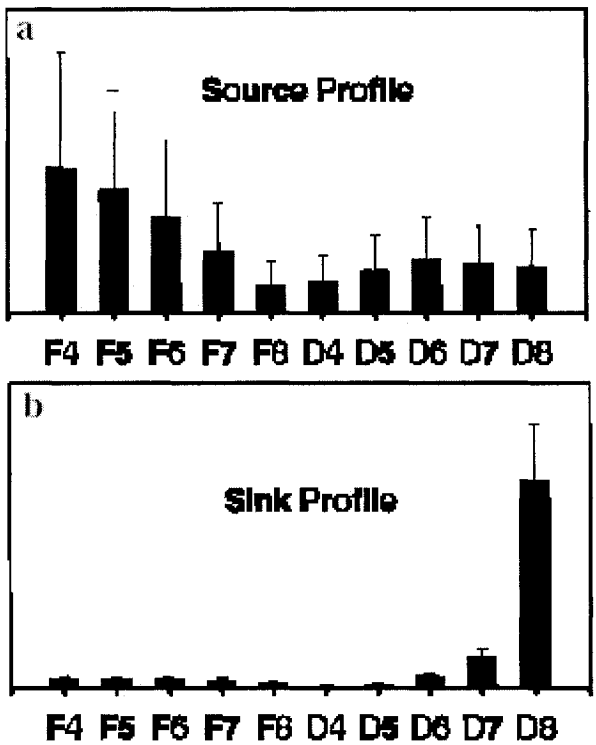


Figure 4.3 PCDD/F homologue profiles from incinerator sources compared to soil sinks in the US.

Concentrations for the source profile are averaged from 12 incinerator profiles, and from 170 soil samples in the US for the sink profile. Standard error bars are shown. PCDFs are denoted as "F" and PCDDs denoted as "D" and number indicate chlorination levels. (Figure adopted from Baker and Hites 2000).

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6.0 Appendix

Appendix 1.1 PCDD/F and PCB homologue breakdown of emissions from the smelter.

(a) PCDD/F and (b) PCB emissions were reported from the electrolysis chambers, as measured by the Quebec Ministry of the Environment, August through November in 2002 (n=6). Concentrations were expressed in volumetric emission rates (TEQ), and were extrapolated to annual releases.

(a)

PCDD/F homologue (pg)	Dates 08_02	08_02	09_02	10_02	11_02	12_02	avg
2378-TCDF	490	175	146.67	266.67	170	173.33	236.95
12378-PeCDF	315	76	213	181.6	125	100	168.43
23478-PeCDF	666.67	352.5	343.33	443.33	261.67	240	384.58
123478-HxCDF	993.33	387	666.6	553.33	383.33	336.67	553.38
123678-HxCDF	273.33	132.5	166.67	133.33	107.33	77.33	148.42
123789-HxCDF	102.67	49.1	49	60	37.67	19	52.91
234678-HxCDF	51	15.5	26.67	23.67	15.33	19.6	25.30
1234678-HpCDF	86	59.77	50.67	54	44.33	28.33	53.85
1234789-HpCDF	30.67	20.8	18.33	15.67	12.67	7.53	17.61
OCDF	44	23	18	39.7	18.33	21.33	27.39
2378-TCDD	88.67	96.5	54.67	67.67	51.67	47.33	67.75
12378-PeCDD	121.67	132	71.67	93.33	100	52.17	95.14
123478-HxCDD	22	7	12.33	17.67	20.67	13	15.45
123678-HxCDD	49.67	38.5	25.67	32.33	37	20.67	33.97
123789-HxCDD	39.67	28	19.33	27.67	28.67	17.33	26.78
1234678-HpCDD	16	18.27	10.33	11.1	11.97	7.97	12.61
OCDD	3.33	2.75	2.03	5.23	2.57	2.23	3.02
total TEQ (pg)	3393.68	1614.19	1894.97	2026.3	1428.21	1183.82	1923.53
ng/m^3	0.199	0.107	0.108	0.115	0.08	0.067	0.11
PCDD/F-TEQ g / year	5.2	2.75	2.9	3.2	2.2	1.68	2.99

(b)

PCB homologue (ng)	Dates 08_02	08_02	09_02	10_02	11_02	12_02	avg
TRI-CB	18.33	5.00	13.50	12.67	8.60	3.97	10.34
TETRA-CB	17.00	0.00	9.50	9.07	7.90	3.10	7.76
PENTA-CB	11.00	0.00	5.80	7.20	6.20	3.40	5.60
HEXA-CB	12.67	0.00	6.60	5.63	7.20	3.60	5.95
HEPTA-CB	17.00	0.00	7.60	9.43	7.80	5.10	7.82
OCTA-CB	23.67	0.00	8.45	9.73	8.60	4.37	9.14
NONA-CB	37.33	16.00	13.50	14.43	11.70	6.93	16.65
DECA-CB	273.33	150.00	92.50	108.00	56.70	34.33	119.14
total PCB (ng)	410.33	170.50	157.45	176.17	114.80	64.80	182.34
ug/m^3	0.02	0.01	0.01	0.01	0.01	0.00	0.01
kg/year	0.60		0.24	0.27		0.08	0.30

(Hince, Noranda Inc., Personal communication)

Appendix 2.1 Prevailing wind direction in 2000, 2001 and 2002 in close proximity to the smelter expressed as monthly and annual averages.

Monthly and annual averages, standard deviations (SD), and standard errors (SE) for each month are shown. Direction of Maximum Gust (in 10's of Degrees) is reported in the direction (true or geographic, not magnetic) from which the wind blows. For example, "9" indicates 90 degrees true or an east wind, and 36 indicates 360 degrees true or a wind blowing from the geographic north pole. This value is only reported if the maximum gust speed exceeds 29 km/hr. Data is from a wind station in Sherbrooke Quebec which has the weather station reporting such data in closest proximity to Danville.

(Environment Canada, 2005)

	2000	2001	2002
Jan	25.71	28.67	25.71
Feb	24.53	25.94	25.07
Mar	25.28	20.41	23.05
April	21.75	26.00	24.73
May	22.89	21.32	24.25
June	23.65	25.31	25.09
July	21.22	24.08	25.50
Aug	24.92	24.90	26.00
Sept	27.08	26.00	25.18
Oct	24.18	23.21	23.25
Nov	24.60	25.85	23.44
Dec	21.88	26.09	23.82
avg	23.97	24.81	24.59
SD	1.76	2.27	1.01
SE	0.51	0.65	0.29

Appendix 2.2 Wind direction in 2000 in close proximity to the smelter expressed daily for each month and monthly averages. Standard deviations (SD) and standard errors (SE) for each month are shown. Direction of Maximum Gust (10's of degrees) is reported, which is the direction (true or geographic, not magnetic) from which the wind blows. For example, "9" indicates 90 degrees true or an east wind, and 36 indicates 360 degrees true or a wind blowing from the geographic north pole. This value is only reported if the maximum gust speed exceeds 29 km/hr. Data is from a wind station in Sherbrooke Quebec which has the weather station reporting such data in closest proximity to Danville.

(Environment Canada, 2005)

Day	Jan	Feb	Mar	April	May	June	July	Aug	Sept	Oct	Nov	Dec
1	27	28	16	27	24	28	27	29	28	17	27	27
2	23	28	28	26	25	28	29	30	26	25	29	28
3	30	27	27	29	28	28	28	24	27	25	16	24
4	28	18	28	23	28	28	28	26	33	28	24	21
5	26	34	16	28	23	25	27	25	29	16	5	29
6	25	25	25	27	31	12	28	27	23	27	28	22
7	27	26	27	19	16	20	29	18	18	26	25	3
8	27	21	19	12	30	27	22	28	24	28	29	28
9	21	19	21	25	26	28	30	27	17	7	28	2
10	19	13	30	27	10	27	15		25	24		27
11	27	26	16	28	6	25	19		27	27		24
12	24	29	14	29	28		24			29		27
13	28	28	23	15	26							24
14	28	29	27	29	27							29

Day	Jan	Feb	Mar	April	May	June	July	Aug	Sept	Oct	Nov	Dec
14	28	29	27	29	27							29
15			29	27	28							35
16			28		27							27
17			16		27							28
18			25		22							
19			27		33							
20			13		26							
21			25		27							
22			27		26							
23					19							
24					19							
avg	25.71	25.07	23.05	24.73	24.25	25.09	25.50	26.00	25.18	23.25	23.44	23.82
SD	3.02	5.48	5.56	5.28	6.33	4.97	4.62	3.54	4.64	6.58	8.02	8.63
SE	0.81	1.47	1.19	1.36	1.29	1.50	1.33	1.18	1.40	1.90	2.67	2.09

Appendix 2.3 Wind direction in 2001 in close proximity to the smelter expressed daily for each month and monthly averages. Standard deviations (SD) and standard errors (SE) for each month are shown. Direction of Maximum Gust (10's of degrees) is reported, which is the direction (true or geographic, not magnetic) from which the wind blows. For example, "9" indicates 90 degrees true or an east wind, and 36 indicates 360 degrees true or a wind blowing from the geographic north pole. This value is only reported if the maximum gust speed exceeds 29 km/hr. Data is from a wind station in Sherbrooke Quebec which has the weather station reporting such data in closest proximity to Danville.

(Environment Canada, 2005)

Day	Jan	Feb	Mar	April	May	June	July	Aug	Sept	Oct	Nov	Dec
1	29	28	4	17	28	19	25	26	31	24	27	28
2	25	26	4	14	26	25	20	23	34	25	36	26
3	32	28	29	29	29	28	22	26	27	26	29	21
4		27	30	30	26	29	26	27	28	28	32	25
5		29	29	29	28	25	28	21	29	27	29	27
6		28	13	35	31	20	25	26	28	13	31	29
7		25	24	29	30	29		27	13	15	29	29
8		21	28	18	35	28	34	18	18	25	27	27
9		25	28	27	2	20	23	26		12	26	23
10		27	12	27	16	28	24	29		25	18	27
11		28	13	27	4	18	27			25	15	25
12		29	27	20	14	27	24			27	10	
13		13	26	34	9	26	34			19	27	
14		28	25	28	18	27	1			29		

Day	Jan	Feb	Mar	April	May	June	July	Aug	Sept	Oct	Nov	Dec
15		26	27	28	17	30				18		
16		27	18	24	12	26				24		
17			10		25					23		
18					27					28		
19					28					28		
20												
21												
avg	28.67	25.94	20.41	26.00	21.32	25.31	24.08	24.90	26.00	23.21	25.85	26.09
SD	3.51	3.97	9.15	5.93	9.61	3.89	8.07	3.28	6.97	5.24	7.26	2.47
SE	2.03	0.99	2.22	1.48	2.20	0.97	2.16	1.04	2.46	1.20	2.01	0.74

Appendix 2.4 Wind direction in 2002 in close proximity to the smelter expressed daily for each month and monthly averages. Standard deviations (SD) and standard errors (SE) for each month are shown. Direction of Maximum Gust (10's of degrees) is reported, which is the direction (true or geographic, not magnetic) from which the wind blows. For example, "9" indicates 90 degrees true or an east wind, and 36 indicates 360 degrees true or a wind blowing from the geographic north pole. This value is only reported if the maximum gust speed exceeds 29 km/hr. Data is from a wind station in Sherbrooke Quebec which has the weather station reporting such data in closest proximity to Danville.

(Environment Canada, 2005)

Day	Jan	Feb	Mar	April	May	June	July	Aug	Sept	Oct	Nov	Dec
1	27	28	16	27	24	28	27	29	28	17	27	27
2	23	28	28	26	25	28	29	30	26	25	29	28
3	30	27	27	29	28	28	28	24	27	25	16	24
4	28	18	28	23	28	28	28	26	33	28	24	21
5	26	34	16	28	23	25	27	25	29	16	5	29
6	25	25	25	27	31	12	28	27	23	27	28	22
7	27	26	27	19	16	20	29	18	18	26	25	3
8	27	21	19	12	30	27	22	28	24	28	29	28
9	21	19	21	25	26	28	30	27	17	7	28	2
10	19	13	30	27	10	27	15		25	24		27
11	27	26	16	28	6	25	19		27	27		24
12	24	29	14	29	28		24			29		27
13	28	28	23	15	26							24
14	28	29	27	29	27							29

Day	Jan	Feb	Mar	April	May	June	July	Aug	Sept	Oct	Nov	Dec
15			29	27	28							35
16			28		27							27
17			16		27							28
18			25		22							
19			27		33							
20			13		26							
21			25		27							
22			27		26							
23					19							
24					19							
avg	25.71	25.07	23.05	24.73	24.25	25.09	25.50	26.00	25.18	23.25	23.44	23.82
SD	3.02	5.48	5.56	5.28	6.33	4.97	4.62	3.54	4.64	6.58	8.02	8.63
SE	0.81	1.47	1.19	1.36	1.29	1.50	1.33	1.18	1.40	1.90	2.67	2.09

Appendix 2.5 The division of coeluted PCBs for individual PCB concentration determination.

Coeluted PCB	Individual PCB concentration determination[a]	Homologue group designation
PCB 54-29:		
PCB-29	0.5 * [PCB-54-29]	Trichlorobiphenyl
PCB-54	0.5 * [PCB-54-29]	Tetrachlorobiphenyl
PCB 33-20-53:		
PCB-53	0.33 * [PCB-33-20-53]	Tetrachlorobiphenyl
PCB 33-20	0.66 * [PCB-33-20-53]	Trichlorobiphenyl
PCB 70-76-98:		
PCB 70-76	0.66 * [PCB 70-76-98]	Tetrachlorobiphenyl
PCB-98	0.33 * [PCB 70-76-98]	Pentachlorobiphenyl
PCB 91-55		
PCB-91	0.5 * [PCB 91-55]	Pentachlorobiphenyl
PCB-55	0.5 * [PCB 91-55]	Tetrachlorobiphenyl
PCB 81-87:		
PCB-81	0.5 * [PCB 81-87]	Tetrachlorobiphenyl
PCB-87	0.5 * [PCB 81-87]	Pentachlorobiphenyl
PCB 107-147:		
PCB-107	0.5 * [PCB 107-147]	Pentachlorobiphenyl
PCB-147	0.5 * [PCB 107-147]	Hexachlorobiphenyl
PCB 114-134-131:		
PCB-114	0.33 * [PCB 114-134-131]	Pentachlorobiphenyl
PCB 134-131	0.66 * [PCB 114-134-131]	Hexachlorobiphenyl
PCB 153-132-105:		
PCB-105	0.33 * [PCB 153-132-105]	Pentachlorobiphenyl
PCB 153-132	0.66 * [PCB 153-132-105]	Hexachlorobiphenyl
PCB 141-179:		
PCB-141	0.5 * [PCB 141-179]	Hexachlorobiphenyl
PCB-179	0.5 * [PCB 141-179]	Heptachlorobiphenyl
PCB 176-130:		
PCB-176	0.5 * [PCB 176-130]	Hexachlorobiphenyl
PCB-130	0.5 * [PCB 176-130]	Heptachlorobiphenyl

Coeluted PCB	Individual PCB concentration determination[a]	Homologue group designation
PCB 202-171-156:		
PCB-156	0.33 * [PCB 202-171-156]	Hexachlorobiphenyl
PCB-171	0.33 * [PCB 202-171-156]	Heptachlorobiphenyl
PCB-202	0.33 * [PCB 202-171-156]	Octachlorobiphenyl
PCB 157-200:		
PCB-157	0.5 * [PCB 157-200]	Hexachlorobiphenyl
PCB-200	0.5 * [PCB 157-200]	Octachlorobiphenyl
PCB 195-208:		
PCB-195	0.5 * [PCB 195-208]	Octachlorobiphenyl
PCB-208	0.5 * [PCB 195-208]	Nonachlorobiphenyl

[a]Numeric fraction represents the weighted chromatographic distribution of each PCB congener within the coeluted peak. It is multiplied by the coeluted PCB concentration to give individual PCB concentration.

Appendix 2.6 Z-scores of PCB congeners and OCs tested using the sample extraction method from The National Wildlife Research Centre (Won et al. 2001) as part of the NIST interlaboratory round robin.

(Kucklick al. 2004)

Accuracy (z-score) and precision (p-score) were classified as follows: $|z| \leq 2$ satisfactory; $2 \leq |z| \leq 3$ questionable; $|z| \leq 3$ unsatisfactory.

Compound	z- score (25%)[a]	p- score (15%)[b]
PCB Congener		
28		1.2
31		0.65
44		0.44
49		0.38
52	-0.9	-0.9
66/95	-0.7	-0.7
87	0.6	0.6
99	-0.2	-0.2
101 (+90)	-1.8	-1.8
105	-1.3	-1.3
118	-0.9	-0.9
128	1.8	1.8
138 (+163+164)	-1.0	-1.0
149	-0.02	-0.02
153	-1.5	-1.5
170 (+190)	-0.6	-0.6
180	-1.3	-1.3
183	-1.1	-1.1
187	-0.9	-0.9
194	-1.5	-1.5
195	-1.7	-1.7
201	-0.9	-0.9
206	-0.8	-0.8
209	-0.8	-0.8

Compound	z- score (25%)	p- score (15%)
OC Compound		
4,4'- DDT	3.1	0.84
4,4'-DDE	0.3	0.43
4,4-DDE	4.2	4.82
HCB	0.1	0.16
a-HCH	0.8	0.22
g-HCH		0.34
Dieldrin	0.1	0.38
Mirex	3.2	1.28

[a] z-score = $(x-X)/\sigma$;

where x= laboratory result, X= Exercise assigned value, and σ = target value for standard deviation (25%)

[b] p-score = CV_{lab}/CV_{target}

where CV is the coefficient of variance. CV_{target} was assigned 15%.

Appendix 2.7 Replicate PCB concentrations using the column extraction and the ASE.

Sample #573 was used for all replicates. PCB concentrations of each replicate using the column extraction method (Won et al. 2001) (573-1 to 573-8; n=8) and the mean, SD, and SE, and SE as a % of the mean are shown. PCB concentrations for one replicate using the ASE extraction method are also shown.

	Column extraction (n=8)								mean	SD	SE	SE%	ASE (n=1)
PCB	573-1	573-2	573-3	573-4	573-5	573-6	573-7	573-8					573-1
1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4-10	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7-9	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8-5	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
19	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
12-13	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
18	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
15-17	29.82	26.88	0.00	0.00	0.00	5.87	0.00	0.00	7.82	12.85	4.06	51.98	0.00
24-27	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
16-32	90.47	66.38	0.00	0.00	0.00	15.67	32.03	27.00	28.94	33.57	10.62	36.68	0.00
54-29	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
26	225.22	206.42	195.00	171.49	116.83	265.68	100.44	0.00	160.13	84.47	26.71	16.68	0.00
25	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
31-28	716.78	211.87	274.89	195.20	189.90	169.18	345.48	252.90	294.52	179.83	56.87	19.31	309.56
33-20-53	194.29	16.64	0.00	0.00	0.00	74.41	3.81	33.13	40.29	67.29	21.28	52.82	0.00
51	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
22	111.42	83.07	82.85	83.31	74.54	88.37	73.74	0.00	74.66	32.35	10.23	13.70	0.00
45	202.22	0.00	109.26	0.00	0.00	0.00	115.94	0.00	53.43	78.77	24.91	46.62	0.00

	Column extraction (n=8)								mean	SD	SE	SE%	ASE (n=1)
PCB	573-1	573-2	573-3	573-4	573-5	573-6	573-7	573-8					573-1
46	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
52	523.91	67.63	60.24	28.76	105.94	107.55	42.90	50.86	123.47	164.21	51.93	42.06	119.95
49	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
43	156.71	80.77	87.55	66.35	64.13	91.42	72.48	67.14	85.82	30.38	9.61	11.19	0.00
48-47	117.80	79.78	112.75	71.93	109.95	116.08	82.89	75.14	95.79	20.01	6.33	6.61	0.00
44	197.60	48.82	0.00	0.00	10.51	18.42	0.00	12.33	35.96	67.28	21.28	59.17	0.00
59-42	59.36	43.83	44.02	45.79	0.00	44.07	46.48	46.36	41.24	17.43	5.51	13.36	0.00
40	80.29	0.00	0.00	0.00	0.00	0.00	0.00	0.00	10.04	28.39	8.98	89.44	0.00
100	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
63	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
74	313.09	184.79	170.12	132.13	179.16	185.28	123.50	146.18	179.28	59.14	18.70	10.43	0.00
70-76-98	411.21	52.44	11.84	12.71	29.47	112.31	58.21	25.71	89.24	134.15	42.42	47.54	0.00
66	266.72	73.01	64.65	72.51	45.50	101.63	55.96	58.16	92.27	72.42	22.90	24.82	0.00
91-55	116.04	76.45	69.35	56.46	58.75	70.71	73.32	65.10	73.27	18.60	5.88	8.03	0.00
56-60	143.69	77.33	80.61	65.82	66.97	66.88	64.66	0.00	70.75	38.83	12.28	17.36	0.00
92	90.29	0.00	0.00	0.00	0.00	0.00	0.00	0.00	11.29	31.92	10.09	89.44	0.00
84	110.45	0.00	0.00	0.00	0.00	72.27	0.00	0.00	22.84	43.51	13.76	60.23	0.00
101	777.16	159.93	171.38	199.59	181.09	314.98	220.08	199.51	277.97	207.33	65.56	23.59	203.69
99	455.47	229.06	251.68	259.04	251.44	301.26	212.99	273.31	279.28	75.99	24.03	8.60	341.13
119	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
83	0.00	0.00	0.00	0.00	0.00	0.00	55.40	0.00	6.92	19.59	6.19	89.44	0.00
97	178.53	0.00	0.00	11.28	13.81	25.71	0.00	0.00	28.67	61.27	19.38	67.59	0.00
87-81	382.73	1.67	0.00	0.00	28.34	85.83	303.07	72.96	109.32	149.39	47.24	43.21	0.00
85	439.89	386.67	312.83	294.38	340.77	280.74	205.51	245.05	313.23	75.46	23.86	7.62	0.00
136	723.77	475.91	551.45	365.81	431.29	422.53	361.29	404.20	467.03	120.56	38.13	8.16	0.00
110	637.18	79.76	35.65	44.31	81.53	180.58	101.63	85.37	155.75	199.43	63.06	40.49	110.69
82	67.14	0.00	0.00	0.00	0.00	0.00	0.00	0.00	8.39	23.74	7.51	89.44	0.00
151	106.05	61.05	57.04	60.74	57.64	93.47	53.36	53.10	67.80	20.22	6.39	9.43	0.00
135-144	95.22	117.11	127.62	60.31	107.30	89.06	25.93	45.60	83.52	36.06	11.40	13.65	0.00
147-107	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

	Column extraction (n=8)								mean	SD	SE	SE%	ASE (n=1)
PCB	573-1	573-2	573-3	573-4	573-5	573-6	573-7	573-8					573-1
149	479.20	93.41	108.05	101.19	132.39	226.92	153.37	115.59	176.26	129.62	40.99	23.26	0.00
118	1500.18	846.65	939.44	970.86	891.07	1018.52	878.31	968.06	1001.64	209.16	66.14	6.60	996.25
133	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
114-134-131	190.97	276.54	157.47	206.76	222.53	273.20	283.47	252.70	232.96	45.85	14.50	6.22	368.99
146	1381.86	1263.91	1329.67	1320.68	1276.87	1578.95	1578.44	1817.31	1443.46	195.72	61.89	4.29	1388.58
153-132-105	8963.59	7877.80	8334.48	8668.21	8062.54	8878.90	8447.82	8631.22	8483.07	379.91	120.14	1.42	9154.43
141-179	131.96	26.55	29.87	75.71	65.30	160.74	47.39	26.43	70.49	50.76	16.05	22.77	0.00
137	46.98	0.00	0.00	40.15	0.00	0.00	42.93	43.42	21.69	23.25	7.35	33.91	0.00
176-130	139.84	131.16	134.35	133.08	134.27	113.58	123.24	129.75	129.91	8.11	2.56	1.97	0.00
138-163	5108.60	4399.62	4736.23	4923.24	4603.48	4691.30	4688.39	4744.59	4736.93	210.08	66.43	1.40	5439.31
158	168.39	180.95	141.76	166.29	190.77	0.00	211.91	167.28	153.42	65.28	20.64	13.46	0.00
129	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
178	868.78	764.66	823.56	814.45	804.86	764.87	1239.70	806.62	860.94	156.60	49.52	5.75	773.54
175	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
187-182	823.57	679.90	757.74	800.27	809.09	1109.68	813.13	806.99	825.05	124.18	39.27	4.76	891.82
183	421.71	326.76	304.52	389.24	419.40	357.27	392.74	288.63	362.53	51.40	16.26	4.48	332.49
128	238.53	167.19	173.97	255.61	150.13	134.28	166.38	175.80	182.74	42.20	13.35	7.30	196.15
167	169.07	176.22	192.27	350.42	248.43	177.05	342.92	204.49	232.61	74.66	23.61	10.15	495.70
185	0.00	0.00	0.00	0.00	0.00	34.42	0.00	0.00	4.30	12.17	3.85	89.44	0.00
174	145.36	53.60	79.36	92.80	106.37	289.92	61.86	79.94	113.65	76.69	24.25	21.34	87.90

	Column extraction (n=8)								mean	SD	SE	SE%	ASE (n=1)
PCB	573-1	573-2	573-3	573-4	573-5	573-6	573-7	573-8					573-1
177	328.91	246.57	287.64	342.76	334.34	429.37	279.18	366.36	326.89	56.87	17.98	5.50	395.56
202-171-156	792.72	542.15	629.40	755.30	685.97	813.39	720.11	716.18	706.90	88.56	28.00	3.96	720.40
173	0.00	0.00	0.00	0.00	0.00	0.00	70.67	0.00	8.83	24.99	7.90	89.44	0.00
157-200	0.00	0.00	24.81	302.11	0.00	147.30	0.00	0.00	59.28	110.50	34.94	58.95	0.00
172	440.20	395.30	446.61	437.53	401.08	398.69	396.32	415.14	416.36	21.79	6.89	1.66	478.52
197	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
180	6032.38	5475.34	5684.20	5863.47	5619.29	6259.18	5965.54	6014.03	5864.18	256.52	81.12	1.38	5974.59
193	184.97	234.74	308.81	254.76	203.40	0.00	208.83	368.41	220.49	107.81	34.09	15.46	0.00
191	0.00	42.60	0.00	68.07	72.18	14.16	32.37	52.04	35.18	28.58	9.04	25.69	149.90
199	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
170-190	2412.19	2286.97	2174.89	2437.01	2343.65	2547.60	2619.49	2777.11	2449.86	192.88	61.00	2.49	3027.74
198	0.00	0.00	0.00	0.00	0.00	78.93	49.64	36.26	20.60	30.73	9.72	47.17	0.00
201	915.31	858.32	880.72	858.97	870.34	1278.04	913.43	929.82	938.12	140.03	44.28	4.72	905.05
203-196	367.24	324.71	330.78	347.17	327.44	801.01	363.30	367.61	403.66	161.55	51.09	12.66	349.36
189	0.00	75.54	89.89	62.41	92.79	94.16	96.02	89.25	75.01	32.37	10.24	13.65	0.00
208-195	267.55	231.41	200.65	204.77	199.09	387.05	251.28	236.25	247.26	61.69	19.51	7.89	194.19
207	0.00	0.00	41.27	39.88	0.00	78.04	45.00	0.00	25.52	29.75	9.41	36.86	0.00
194	1025.00	970.49	958.32	932.87	951.13	1281.69	1025.62	1053.19	1024.79	112.15	35.47	3.46	1025.48
205	0.00	71.95	69.68	67.86	54.93	77.80	66.62	69.88	59.84	25.02	7.91	13.22	0.00
206	150.19	143.06	140.05	147.07	129.26	386.68	156.06	140.49	174.11	86.26	27.28	15.67	84.60
209	229.96	195.76	202.04	181.78	205.94	230.84	225.64	204.65	209.58	17.66	5.59	2.67	184.95
total PCB	41945.69	32267.07	33583.29	34910.66	33153.25	38513.45	35788.24	35334.57	35687.03	3172.17	1121.53	3.14	34700.53

Appendix 2.8 Detection limits of PCB congeners, homologue groups and total ∑PCB.

Method detection limits (pg/g) were calculated as an average of the method blanks (n=18) ± 2*SD and the detection limits were reported as 2*SD, as the data had been blank subtracted at the onset of analysis.

PCB congener	DL
1	0.00
3	0.00
4-10	0.00
7-9	0.00
6	0.00
8-5	0.00
19	0.00
12-13	126.66
18	279.74
15-17	185.27
24-27	0.00
16-32	89.18
54-29	420.45
26	111.42
25	49.14
31-28	190.88
33-20-53	111.82
51	0.00
22	52.47
45	80.06
46	67.34
52	64.47
49	0.00
43	38.83
48-47	79.44
44	56.42
59-42	28.15
40	87.70
100	61.29
63	0.00
74	57.12
70-76-98	632.34
66	49.16
91-55	31.79

PCB congener	DL
56-60	319.61
92	50.31
84	48.71
101	82.69
99	32.00
119	0.00
83	27.20
97	47.81
87-81	42.34
85	50.49
136	55.90
110	44.66
82	31.41
151	32.67
135-144	50.16
147-107	92.75
149	68.93
118	84.50
133	172.03
114-134-131	117.58
146	45.56
153-132-105	114.19
141-179	36.25
137	0.00
176-130	12.66
138-163	102.16
158	23.05
129	14.15
178	28.72
175	0.00
187-182	26.48
183	0.00
128	16.53
167	141.09
185	0.00
174	26.41
177	24.78
202-171-156	45.39
173	28.10
157-200	524.56
172	0.00
197	0.00
180	86.18
193	15.43
191	109.82

PCB congener	DL
199	0.00
170-190	260.35
198	0.00
201	22.35
203-196	32.02
189	17.54
208-195	27.28
207	44.32
194	28.14
205	0.00
206	24.72
209	33.39
PCB homologue	
mono+di	165.56
tri	686.58
tetra	645.92
penta	442.87
hexa	510.51
hepta	342.90
octa	243.53
nona	58.60
deca	33.39
Total PCB	1759.22

Appendix 2.9 Detection limits of organochlorine pesticides.

Method detection limits (pg g^{-1}) were calculated as an average of the method blanks (n=18) ± 2*SD and the detection limits were reported as 2*SD as the data had been blank subtracted at the onset of analysis.

OC compound	DL
1,3-DCB	14663.05
1,4-DCB	592.79
1,2-DCB	360433.23
1,3,5-TCB	0.00
1,2,4-TCB	2897.53
1,2,3-TCB	0.00
1,2,3,4-TTCB	0.00
PECB	40.17
a-HCH	22.50
HCB	512.84
g-HCH	206.29
Heptachlor	12.68
Aldrin	21.99
Heptachlor Epoxide	23.06
g-Chlordane	46.31
a-Endosulfan	32.84
a-Chlordane	55.99
Dieldrin	32.39
p,p'-DDE	169.81
Endrin	317.46
b-Endosulfan	137.79
p,p'-DDD	27.85
o,p'-DDT	0.00
p,p'-DDT	0.00
Methoxychlor	0.00

Appendix 2.10 Spiking solutions used for the coplanar PCBs and PCDD/F samples, and the batch and sample calibration standards.

PCDD/F Analytical Samples

- 10ul PCDD/F ^{13}C spiking solution (dilution #22C, 50-100pg/ µl)
- 10ul clean up standard solution ^{37}Cl-2,3,7,8-Tetrachlorodibenzo-p-dioxin (dilution #31A, 0.8pg/ µl)
- 5ul PCDD/F instrument performance standard solution (dilution #37A, 100pg/ µl)

PCDD/F HRGC-HRMS Standard

PCDD/F batch calibration standard

- 20ul PCDD/F ^{13}C spiking solution (dilution #22C, 50-100pg/ µl)
- 10ul PCDD/F instrument performance standard solution (dilution #37A, 100pg/ µl)
- 10ul PCDD/F native stock standard solution (Dilution #24B, 20-10-200pg/ µl)
- 20ul clean up standard solution ^{37}Cl-2,3,7,8-Tetrachlorodibenzo-p-dioxin (dilution #31A, 0.8pg/µl)

PCDD/F sample calibration standard

- 20ul PCDD/F ^{13}C spiking solution (dilution #22C, 50-100pg/µl)
- 10ul instrument performance standard solution (dilution #37A, 100pg/µl)

20ul clean up standard solution ^{37}Cl-2,3,7,8-Tetrachlorodibenzo-p-dioxin (dilution #31A, 0.8pg/µl)

NO-PCB Analytical Samples

- 10ul of NO-PCB ^{13}C spiking Solution (dilution #25A, 100pg/µl)
- 5ul NO-PCB Instrument performance standard solution (dilution #36A, PCB-112, 200pg/µl).

NO-PCB HRGC-HRMS Standard

NO-PCB batch calibration standard

- 20ul NO-PCB ^{13}C spiking solution (dilution #35A)
- 20ul NO-PCB native stock standard solution (Dilution #34A, 10pg/µl)
- 10ul NO-PCB Instrument performance standard solution (dilution #36A, PCB-112, 200pg/µl).

NO-PCB sample calibration standard

- 20ul NO-PCB ^{13}C spiking solution (dilution #35A)
- 10ul NO-PCB Instrument performance standard solution (dilution #36A, PCB-112, 200pg/µl).

Appendix 2.11 Limit of detection (LOD) and limit of quantification (LOQ) for PCDD/F and coplanar PCB samples (N=12).

Sample ID	573			519			560			571		
	pg/g	LOD	LOQ	pg/g	LOD	LOQ	pg/g	LOD	LOQ	pg/g	LOD	LOQ
PCDD/Fs												
2378-TCDF	1.827	0.039	0.039	0.372	0.039	0.039	0.736	0.024	0.024	0.286	0.027	0.027
12378-PeCDF	7.969	0.084	0.084	1.240	0.049	0.049	2.669	0.033	0.033	0.397	0.030	0.030
23478-PeCDF	11.946	0.082	0.082	1.852	0.049	0.049	3.833	0.032	0.032	0.777	0.029	0.029
123478-HxCDF	10.094	0.046	0.046	1.521	0.055	0.055	3.050	0.030	0.030	0.582	0.033	0.033
123678-HxCDF	9.722	0.042	0.042	1.477	0.049	0.049	3.355	0.028	0.028	0.487	0.032	0.032
123789-HxCDF	13.829	0.049	0.049	1.888	0.058	0.058	4.261	0.032	0.032	0.654	0.038	0.038
234678-HxCDF	14.621	0.053	0.053	2.087	0.065	0.065	4.117	0.036	0.036	0.487	0.040	0.040
1234678-HpCDF	9.533	0.064	0.064	1.498	0.029	0.029	3.646	0.034	0.034	0.386	0.029	0.029
1234789-HpCDF	12.313	0.077	0.077	2.027	0.035	0.035	4.266	0.039	0.039	0.376	0.034	0.034
OCDF	35.138	0.063	0.063	4.779	0.043	0.043	10.040	0.042	0.042	0.948	0.033	0.033
2378-TCDD	1.616	0.054	0.054	0.339	0.065	0.065	0.483	0.037	0.037	0.296	0.037	0.037
12378-PeCDD	9.682	0.087	0.087	1.623	0.066	0.066	3.158	0.039	0.039	0.565	0.054	0.054
123478-HxCDD	10.932	0.169	0.169	2.177	0.065	0.065	4.100	0.043	0.043	1.027	0.032	0.032
123678-HxCDD	10.482	0.156	0.156	1.452	0.061	0.061	3.264	0.036	0.036	0.361	0.016	0.016
123789-HxCDD	13.028	0.099	0.099	2.070	0.039	0.039	3.946	0.023	0.023	0.487	0.019	0.019
1234678-HpCDD	11.379	0.085	0.085	1.452	0.062	0.062	3.810	0.036	0.036	0.769	0.041	0.041
OCDD	24.121	0.116	0.116	3.823	0.119	0.119	9.713	0.046	0.046	1.992	0.053	0.053
noPCBs												
Name	**pg/g**	**LOD**	**LOQ**	**pg/g**	**LOD**	**LOQ**	**pg/g**	**LOD**	**LOQ**	**pg/g**	**LOD**	**LOQ**
PCB 77	6.000	0.116	0.310	11.720	0.116	0.308	9.310	0.097	0.258	4.450	0.073	0.195
PCB 126	120.750	0.163	0.434	20.220	0.162	0.431	18.630	0.115	0.308	10.930	0.100	0.267
PCB 169	25.030	0.079	0.211	13.420	0.075	0.201	1.920	0.051	0.136	1.410	0.036	0.096

Sample ID	502			501			566			570		
Name	pg/g	LOD	LOQ	pg/g	LOD	LOQ	pg/g	LOD	LOQ	pg/g	LOD	LOQ
PCDD/Fs												
2378-TCDF	0.000	0.031	0.031	0.244	0.023	0.023	0.111	0.015	0.015	0.631	0.038	0.038
12378-PeCDF	0.390	0.035	0.035	0.186	0.028	0.028	0.184	0.034	0.034	2.844	0.042	0.042
23478-PeCDF	0.812	0.035	0.035	0.575	0.028	0.028	0.316	0.015	0.015	4.017	0.041	0.041
123478-HxCDF	0.501	0.031	0.031	0.289	0.027	0.027	0.247	0.024	0.024	3.430	0.045	0.045
123678-HxCDF	0.452	0.029	0.029	0.175	0.016	0.016	0.169	0.009	0.009	3.420	0.041	0.041
123789-HxCDF	0.435	0.034	0.034	0.241	0.018	0.018	0.218	0.023	0.023	4.459	0.049	0.049
234678-HxCDF	0.339	0.037	0.037	0.175	0.031	0.031	0.190	0.011	0.011	4.215	0.051	0.051
1234678-HpCDF	0.567	0.021	0.021	0.188	0.012	0.012	0.219	0.031	0.031	3.555	0.028	0.028
1234789-HpCDF	0.354	0.010	0.010	0.163	0.023	0.023	0.122	0.019	0.019	3.895	0.032	0.032
OCDF	0.818	0.010	0.010	0.286	0.023	0.023	0.267	0.025	0.025	12.096	0.025	0.025
2378-TCDD	0.182	0.054	0.054	0.213	0.032	0.032	0.000	0.045	0.045	0.556	0.052	0.052
12378-PeCDD	0.477	0.043	0.043	0.377	0.026	0.026	0.000	0.064	0.064	3.255	0.058	0.058
123478-HxCDD	0.928	0.040	0.040	0.816	0.033	0.033	0.723	0.050	0.050	3.730	0.044	0.044
123678-HxCDD	0.467	0.034	0.034	0.311	0.016	0.016	0.000	0.042	0.042	3.576	0.040	0.040
123789-HxCDD	0.355	0.022	0.022	0.321	0.020	0.020	0.249	0.013	0.013	3.648	0.026	0.026
1234678-HpCDD	0.556	0.029	0.029	0.264	0.019	0.019	0.374	0.044	0.044	3.978	0.052	0.052
OCDD	1.906	0.045	0.045	1.374	0.037	0.037	0.954	0.025	0.025	8.729	0.041	0.041
noPCBs												
Name	pg/g	LOD	LOQ	pg/g	LOD	LOQ	pg/g	LOD	LOQ	pg/g	LOD	LOQ
PCB 77	20.480	0.168	0.447	7.050	0.097	0.257	5.470	0.118	0.315	4.650	0.125	0.333
PCB 126	37.070	0.155	0.412	21.530	0.123	0.327	6.300	0.094	0.251	7.620	0.168	0.449
PCB 169	18.850	0.111	0.295	3.900	0.061	0.162	1.270	0.046	0.123	1.480	0.061	0.163

Sample ID	509			569			555			577		
Name	**pg/g**	**LOD**	**LOQ**	**pg/g**	**LOD**	**LOQ**	**pg/g**	**LOD**	**LOQ**	**pg/g**	**LOD**	**LOQ**
PCDD/Fs												
2378-TCDF	0.000	0.027	0.027	0.000	0.035	0.035	0.674	0.045	0.045	6.312	0.027	0.027
12378-PeCDF	0.268	0.039	0.039	0.000	0.041	0.041	2.230	0.064	0.064	0.244	0.047	0.047
23478-PeCDF	0.362	0.038	0.038	0.000	0.039	0.039	3.435	0.062	0.062	0.550	0.042	0.042
123478-HxCDF	0.338	0.032	0.032	0.000	0.034	0.034	3.180	0.038	0.038	0.442	0.024	0.024
123678-HxCDF	0.347	0.029	0.029	0.000	0.031	0.031	3.035	0.035	0.035	0.459	0.021	0.021
123789-HxCDF	0.471	0.034	0.034	0.000	0.036	0.036	4.456	0.041	0.041	1.228	0.014	0.014
234678-HxCDF	0.407	0.018	0.018	0.000	0.039	0.039	4.036	0.045	0.045	0.225	0.027	0.027
1234678-HpCDF	0.399	0.025	0.025	0.165	0.031	0.031	3.752	0.039	0.039	0.567	0.018	0.018
1234789-HpCDF	0.387	0.029	0.029	0.000	0.037	0.037	4.282	0.045	0.045	0.336	0.020	0.020
OCDF	1.021	0.034	0.034	0.473	0.030	0.030	15.393	0.034	0.034	1.663	0.019	0.019
2378-TCDD	0.116	0.025	0.025	0.000	0.061	0.061	0.392	0.020	0.020	0.000	0.043	0.043
12378-PeCDD	0.326	0.068	0.068	0.000	0.063	0.063	3.085	0.060	0.060	0.302	0.031	0.031
123478-HxCDD	0.789	0.054	0.054	0.746	0.043	0.043	3.679	0.063	0.063	0.889	0.039	0.039
123678-HxCDD	0.000	0.050	0.050	0.000	0.040	0.040	3.279	0.058	0.058	0.200	0.036	0.036
123789-HxCDD	0.383	0.013	0.013	0.000	0.025	0.025	3.510	0.037	0.037	0.289	0.023	0.023
1234678-HpCDD	0.493	0.047	0.047	0.300	0.048	0.048	4.386	0.055	0.055	0.621	0.011	0.011
OCDD	1.394	0.045	0.045	0.895	0.049	0.049	9.828	0.046	0.046	1.954	0.021	0.021
noPCBs												
Name	**pg/g**	**LOD**	**LOQ**	**pg/g**	**LOD**	**LOQ**	**pg/g**	**LOD**	**LOQ**	**pg/g**	**LOD**	**LOQ**
PCB 77	2.860	0.103	0.274	3.200	0.071	0.190	5.550	0.080	0.213	8.520	0.105	0.280
PCB 126	3.620	0.093	0.249	4.770	0.096	0.256	7.930	0.101	0.269	6.640	0.114	0.304
PCB 169	1.280	0.047	0.127	1.310	0.038	0.101	1.550	0.045	0.121	2.310	0.057	0.151

Appendix 2.12 Concentrations of reagents on a 48-well plate.

	Well #	Sample	Buffer	BSA		Resorufin in buffer		ER		NADPH		Florescamine in acetonitrile
Standard wells			(ul)	(ul)	Final [BSA] (ug/ml)	(ul)	Final [Resorufin] (nM)	(ul)	Final [ER] (uM)	(ul)	Final NADPH (mM)	(ul)
	1 A-C		-	-	-	-	-	-	-	-	-	-
	1 D-F		-	-	-	-	-	-	-	-	-	-
	2 A-C		135	0	0	0	0	50	1.4	50	0.36	100
	2 D-F		124	10	58.5	1	44.77	50	1.4	50	0.36	100
	3 A-C		113	20	117	2	89.55	50	1.4	50	0.36	100
	3 D-F		91	40	234.02	4	179.10	50	1.4	50	0.36	100
	4 A-C		70	60	351	5	223.88	50	1.4	50	0.36	100
	4 D-F		47	80	468	8	358.20	50	1.4	50	0.36	100
EROD/ protein wells				Microsomes (ul)								
	A 5	blank 1	165	20				50	1.4	0	0	100
	A 6-8	sample 1	115	20				50	1.4	50	0.36	100
	B 5	blank 2	165	20				50	1.4	0	0	100
	B 6-8	sample 2	115	20				50	1.4	50	0.36	100
	C 5	blank 3	165	20				50	1.4	0	0	100
	C 6-8	sample 3	115	20				50	1.4	50	0.36	100
	D 5	blank 4	165	20				50	1.4	0	0	100
	D 6-8	sample 4	115	20				50	1.4	50	0.36	100
	F 5	blank 5	165	20				50	1.4	0	0	100
	F 6-8	sample 5	115	20				50	1.4	50	0.36	100

Appendix 2.13 Formulas for total protein determination derived from a BSA standard curve, and resorufin and EDOD activity derived from a resorufin standard curve.

Calculations used for each plate are outlined (Kennedy and Jones 1994, 1997).

The following calculations were used to determine the EROD activity of the samples for each plate (NWRC, 1997):

1. BSA Standard curve and protein determination (mg)

Fluorescence units (response at 460nm) (y) are plotted against BSA concentrations (ul/ml) (x) and fit using a quadratic polynomial equation: $F = a + bx + cx^2$
a, b and c are coefficients determined by the non-linear regression of the standard curve and these are used for the following math transformations:

Math Transformation
[1] Z = {(b)^2-[4*a-samples fluorescence)]*c}^0.5
[2] Y=(-b+Z)/(2*c)
[3] total proteins = (Y(ug/ml)*(0.335ml)/1000ug/mg
where 0.335 ml = total volume in well

2. Resorufin standard curve and determination of EROD activity (pmolRESOFURIN/min/mg proteins)

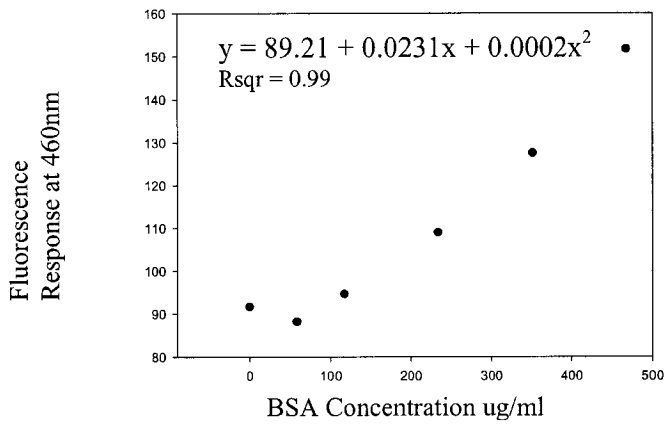
Fluorescence (y) (subtracted with blanks) are plotted against resorufin concentration (nM) (x) and fitted using the equation y=mx+b.

[1] EROD activity
=[resorufin]nM * $335*10^{-6}$L * 1000 pmole $nmol^{-1}$ / min * total proteins (mg)

where resorufin concentration (x) is determined from the standard curve and min is the reaction time (10minutes).

Appendix 2.14 Total protein determination derived from a BSA standard curve plate1.

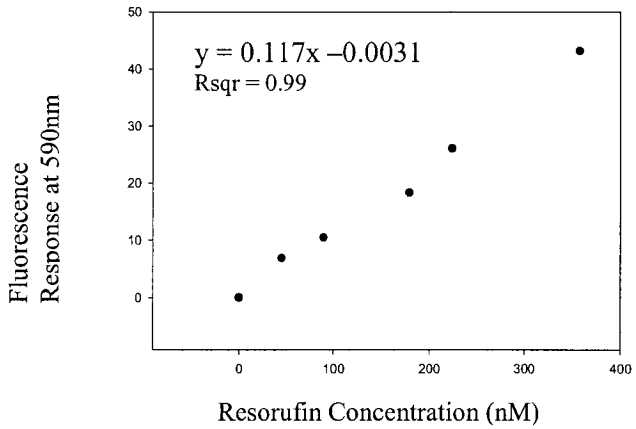
BSA (ug/ml)	Fluorescence (y) avg (n=3)	SE
0	91.62	4.06
58.5	88.16	6.35
117	94.61	6.94
234.02	108.93	7.07
351	127.51	8.32
468	151.64	1.96



sample	FLUORESCENCE replicate	response	Z [1]	Y [2]	[3] total protein in well (mg)
577	1	110.9810	0.1340	277.2220	0.0929
	2	106.8300	0.1210	244.6591	0.0820
	3	109.0860	0.1282	262.7672	0.0880
571	1	97.9360	0.0867	159.0016	0.0533
	2	106.3870	0.1195	240.9744	0.0807
	3	98.3290	0.0885	163.4880	0.0548
566	1	111.3150	0.1350	279.7056	0.0937
	2	123.6030	0.1675	360.9578	0.1209
	3	116.2190	0.1488	314.2665	0.1053
562	1	111.3150	0.1350	279.7056	0.0937
	2	123.6030	0.1675	360.9578	0.1209
	3	116.2190	0.1488	314.2665	0.1053
523	1	105.6900	0.1171	235.0831	0.0788
	2	111.3320	0.1350	279.8315	0.0937
	3	107.2120	0.1222	247.8007	0.0830

Appendix 2.15 Resorufin determination derived from a resorufin standard curve plate 1.

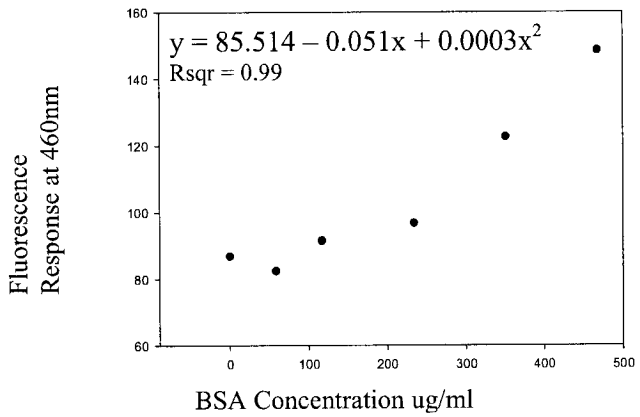
Resorufin (nM) (x)	Fluorescence (y) avg (n=3)	avg-bl	SE
0	0.93	0	0.11
44.78	7.79	6.86	2.90
89.55	11.39	10.46	1.02
179.10	19.22	18.29	1.25
223.88	26.93	25.99	2.86
358.21	44.10	43.17	1.19



sample	blank	replicate	Fluorescence (y) response	(y) - blank	[1] EROD activity	avg (n=3)	SE
577	1.22	1	18.99	17.77	54.80	61.21	3.31
		2	19.25	18.03	63.00		
		3	21.46	20.24	65.84		
571	1.20	1	29.15	27.96	150.29	134.17	18.12
		2	28.82	27.63	97.99		
		3	30.69	29.50	154.22		
566	1.22	1	12.66	11.45	34.99	31.12	2.68
		2	12.18	10.97	25.98		
		3	13.13	11.91	32.40		
562	1.25	1	29.00	27.75	84.80	77.54	5.23
		2	29.70	28.45	67.38		
		3	30.82	29.57	80.43		
523	1.25	1	13.03	11.79	42.86	40.83	2.52
		2	15.59	14.34	43.81		
		3	11.63	10.38	35.82		

Appendix 2.16 Total protein determination derived from a BSA standard curve plate 2.

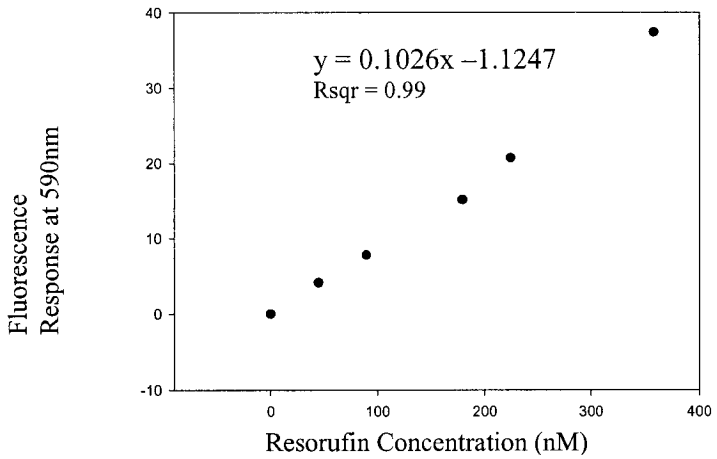
BSA (x) (ug/ml)	Fluorescence (y) avg (n=3)	SE
0	86.79	1.70
58.50	82.38	6.71
117.00	91.50	9.58
234.02	96.77	9.43
351.00	122.56	9.09
468.00	148.38	16.97



sample	FLOURESCENCE replicate	response	Z (1)	Y (2)	[3] total protein (mg)
515	1	117.7230	0.1972	353.7951	0.1185
	2	120.4100	0.2052	367.1511	0.1230
	3	122.3420	0.2108	376.4405	0.1261
567	1	105.6690	0.1562	285.5830	0.0957
	2	98.8400	0.1274	237.4244	0.0795
	3	109.2550	0.1695	307.6025	0.1030
565	1	119.0070	0.2010	360.2438	0.1207
	2	120.5370	0.2056	367.7694	0.1232
	3	114.8600	0.1883	338.9394	0.1135
560	1	106.0760	0.1578	288.1749	0.0965
	2	114.8370	0.1882	338.8172	0.1135
	3	120.3240	0.2049	366.7317	0.1229
557	1	101.0840	0.1375	254.3682	0.0852
	2	91.7430	0.0878	171.4427	0.0574
	3	99.9500	0.1325	245.9682	0.0824
504	1	108.1810	0.1656	301.1920	0.1009
	2	111.4410	0.1770	320.2203	0.1073
	3	115.8240	0.1913	344.0188	0.1152
537	1	82.6120			
	2	82.9860			
	3	82.9860			

Appendix 2.17 Resorufin determination derived from a resorufin standard curve plate 2.

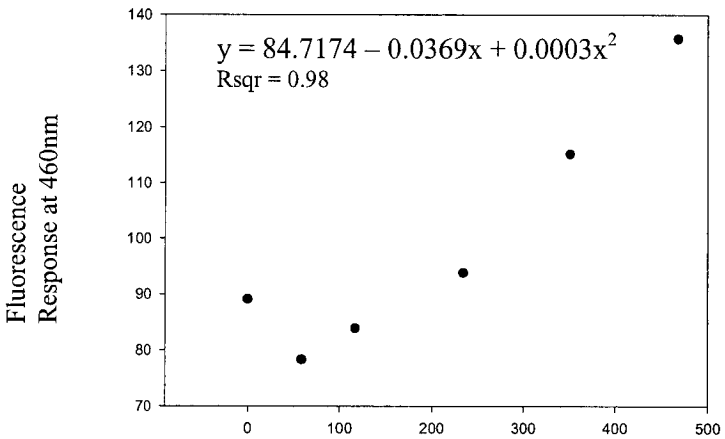
Resorufin (nM) (x)	Fluorescence (y) avg (n=3)	avg-bl	SE
0	1.34	0.00	0.06
44.78	5.46	4.12	0.32
89.55	9.11	7.78	0.64
179.10	16.46	15.13	1.14
223.88	22.05	20.71	2.13
358.21	38.71	37.37	2.08



sample	blank	Fluorescence replicate	(y) response	(y) - blank	[1] EROD activity	avg (n=3)	SE
515	2.09	1	11.33	9.24	28.55	26.57	1.38
		2	9.97	7.88	23.90		
		3	11.49	9.40	27.26		
567	1.62	1	25.53	23.90	85.42	96.31	9.28
		2	28.46	26.83	114.77		
		3	28.51	26.89	88.75		
565	1.79	1	20.68	18.88	54.13	54.62	0.95
		2	20.77	18.98	53.27		
		3	20.30	18.51	56.45		
560	1.57	1	14.27	12.71	46.77	44.82	1.03
		2	15.49	13.92	43.28		
		3	17.15	15.59	44.41		
557	1.53	1	23.08	21.55	86.90	104.35	20.36
		2	25.90	24.37	144.95		
		3	20.90	19.37	81.21		
504	1.98	1	43.22	41.24	137.09	128.82	4.61
		2	42.98	41.00	128.22		
		3	43.62	41.64	121.15		

Appendix 2.18 Total protein determination derived from a BSA standard Plate 3.

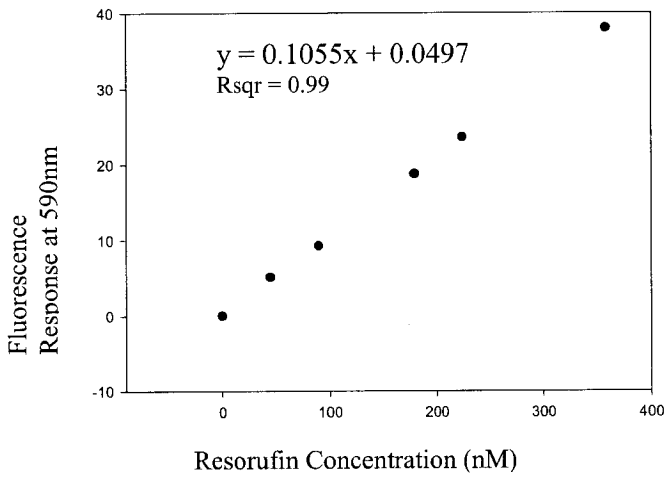
BSA (x) (ug/ml)	Fluorescence (y) avg (n=3)	SE
0	89.06	3.10
58.5	78.29	8.23
117	83.86	9.18
234.02	93.83	8.06
351	115.13	7.02
468	135.70	12.43



sample	FLOURESCENCE replicate	response	Z [1]	Y [2]	[3] total protein (mg)
502	1	126.5650	0.2271	440.0099	0.1474
	2	127.1280	0.2286	442.4809	0.1482
	3	128.9440	0.2333	450.3442	0.1509
583	1	99.0160	0.1361	288.3034	0.0966
	2	94.8400	0.1162	255.2002	0.0855
	3	96.0800	0.1225	265.5909	0.0890

Appendix 2.19 Resorufin determination derived from a resorufin standard curve plate 3.

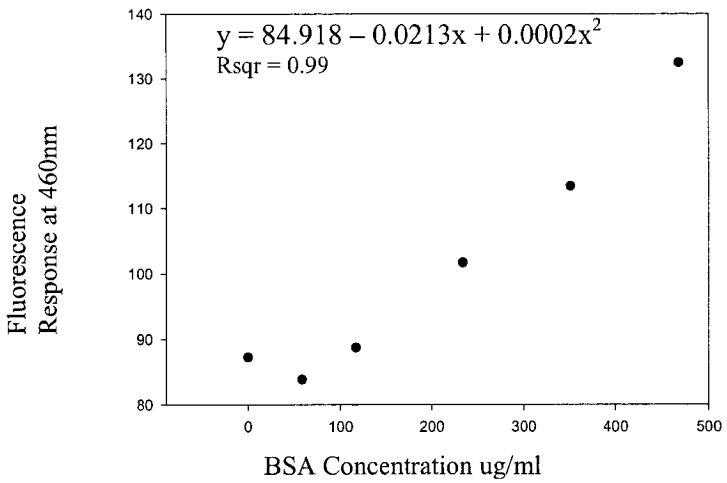
Resorufin (nM) (x)	Fluorescence (y) avg (n=3)	avg-bl	SE
0	1.07	0.00	0.10
44.78	6.21	5.14	0.16
89.55	10.36	9.29	0.72
179.10	19.85	18.77	1.45
223.88	24.66	23.58	2.50
358.21	39.04	37.97	2.39



sample	blank	Fluorescence replicate	(y) response	(y) - blank	[1] EROD activity	avg (n=3)	SE
502	3.51	1	50.81	47.30	101.79	97.66	3.08
	3.51	2	50.04	46.53	99.56		
	3.51	3	47.09	43.59	91.63		
583	1.43	1	16.21	14.78	41.77	59.58	5.67
	1.43	2	19.50	18.06	55.32		
	1.43	3	19.25	17.82	53.21		

Appendix 2.20 Total protein determination derived from a BSA standard curve plate 4.

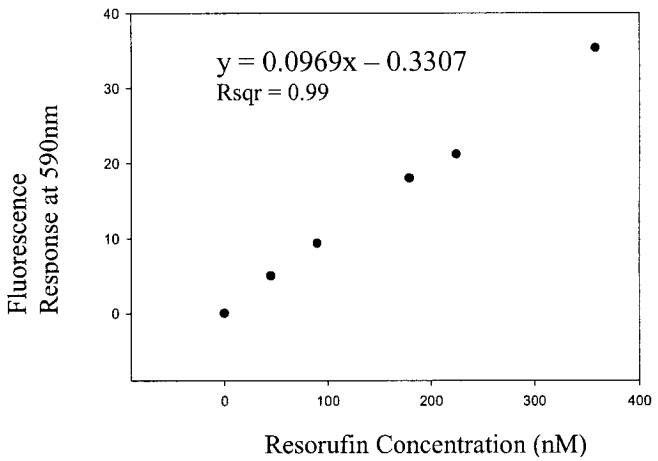
BSA (x) (ug/ml)	Fluorescence (y) avg (n=3)	SE
0.00	87.20	5.13
58.50	83.84	6.92
117.00	88.68	9.58
234.02	101.69	7.17
351.00	113.37	10.25
468.00	132.43	6.80



Sample	FLOURESCENCE replicate	response	Z (1)	Y (2)	[3] total protein (mg)
501	1	104.5710	0.1272	264.7357	0.0887
	2	114.4340	0.1551	334.6029	0.1121
	3	104.5970	0.1273	264.9400	0.0888
589	1	111.1450	0.1464	312.7894	0.1048
	2	114.3250	0.1549	333.8997	0.1119
	3	117.0880	0.1618	351.3484	0.1177

Appendix 2.21 Resorufin determination derived from a resorufin standard curve plate 4.

Resorufin (nM) (x)	Fluorescence (y) avg (n=3)	avg-bl	SE
0	1.14	0.001	0.11
44.78	6.12	4.98	1.13
89.55	10.48	9.34	1.16
179.10	19.10	17.96	1.76
223.88	22.30	21.16	1.14
358.21	36.46	35.32	1.61



sample	blank	replicate	Fluorescence (y) response	(y) - blank	[1] EROD activity	avg (n=3)	SE
501	1.30	1	17.07	15.77	60.17	55.00	5.16
	1.30	2	16.12	14.82	44.68		
	1.30	3	17.08	15.77	60.15		
589	1.29	1	8.73	7.44	23.45	19.92	1.79
	1.29	2	7.31	6.03	17.60		
	1.29	3	7.99	6.70	18.72		

Appendix 3.1 Mean relative abundance of PCB congeners.

Relative abundances in the 2002 deer are calculated as a % of total PCBs. These are shown in descending order and are expressed as an average of total (n=43), an average of deer samples located near (<5km, n=10), and far from the smelter (>15km, n=15).

PCB	Total	PCB	Near	PCB	Far
153-132-105	14.55	153-132-105	15.60	153-132-105	14.87
138-163	7.63	138-163	9.87	180	6.70
180	7.13	180	8.54	138-163	6.54
118	4.51	157-200	6.58	118	5.52
157-200	4.04	118	3.85	15-17	4.09
31-28	3.54	170-190	3.67	31-28	4.05
170-190	3.16	201	3.09	146	2.74
146	3.03	31-28	2.65	170-190	2.49
136	2.70	146	2.62	99	2.31
201	2.39	101	2.47	43	2.29
15-17	2.22	187-182	1.69	136	2.24
101	2.19	136	1.65	74	2.06
26	2.16	202-171-156	1.63	45	1.97
99	2.05	82	1.47	201	1.90
74	1.76	99	1.47	26	1.70
85	1.50	207	1.45	167	1.57
202-171-156	1.43	178	1.44	18	1.56
187-182	1.40	26	1.39	85	1.50
18	1.40	18	1.31	33-20-53	1.45
43	1.37	33-20-53	1.31	101	1.45
48-47	1.31	194	1.25	207	1.42
133	1.18	74	1.10	157-200	1.35
66	1.17	85	1.05	202-171-156	1.32
207	1.14	52	1.05	133	1.32
33-20-53	1.13	158	0.92	54-29	1.29
194	1.12	114-134-131	0.91	44	1.18
178	1.09	15-17	0.89	114-134-131	1.17
114-134-131	1.06	66	0.79	48-47	1.16
167	1.00	133	0.79	66	1.14
44	0.98	56-60	0.78	191	1.13
45	0.94	167	0.77	110	1.06
209	0.88	87-81	0.72	194	0.96
110	0.87	177	0.72	187-182	0.95
191	0.86	193	0.71	206	0.92
82	0.84	110	0.69	209	0.88
177	0.79	43	0.69	52	0.76
52	0.79	149	0.67	87-81	0.76

PCB	Total	PCB	Near	PCB	Far
158	0.73	203-196	0.66	158	0.76
206	0.71	208-195	0.66	16-32	0.75
87-81	0.71	48-47	0.66	22	0.74
56-60	0.70	70-76-98	0.65	128	0.73
16-32	0.66	191	0.64	203-196	0.72
203-196	0.65	147-107	0.63	56-60	0.72
54-29	0.60	44	0.58	177	0.67
149	0.59	128	0.55	82	0.54
193	0.58	209	0.54	193	0.5
208-195	0.56	45	0.49	135-144	0.53
70-76-98	0.54	63	0.48	178	0.53
22	0.52	172	0.48	149	0.52
135-144	0.50	183	0.45	174	0.52
128	0.48	151	0.45	92	0.49
151	0.36	206	0.40	70-76-98	0.46
174	0.35	22	0.37	208-195	0.34
92	0.31	174	0.35	63	0.34
147-107	0.31	16-32	0.30	46	0.27
63	0.28	176-130	0.29	141-179	0.23
172	0.28	135-144	0.26	183	0.20
183	0.27	91-55	0.24	189	0.18
176-130	0.22	84	0.22	40	0.17
137	0.21	92	0.21	151	0.17
141-179	0.21	141-179	0.20	59-42	0.16
91-55	0.20	40	0.15	172	0.15
59-42	0.18	137	0.14	119	0.14
84	0.17	54-29	0.13	83	0.12
40	0.16	97	0.13	137	0.12
97	0.14	59-42	0.12	91-55	0.10
189	0.10	199	0.09	176-130	0.10
205	0.08	83	0.09	198	0.07
46	0.07	189	0.07	205	0.06
83	0.07	205	0.05	185	0.05
119	0.06	198	0.02	97	0.03
199	0.05	173	0.01	84	0.01
198	0.04	185	0.00	1	0
25	0.03	1	0	3	0
185	0.01	3	0	4-10	0
173	0	4-10	0	7-9	0
1	0	7-9	0	6	0
3	0	6	0	8-5	0
4-10	0	8-5	0	19	0
7-9	0	19	0	12-13	0
6	0	12-13	0	24-27	0
8-5	0	24-27	0	25	0
19	0	25	0	51	0

PCB	Total	PCB	Near	PCB	Far
12-13	0	51	0	49	0
24-27	0	46	0	100	0
51	0	49	0	147-107	0
49	0	100	0	129	0
100	0	119	0	175	0
129	0	129	0	173	0
175	0	175	0	197	0
197	0	197	0	199	0

Appendix 3.2 Results for the regression between PCB concentration and distance from the smelter in deer from 1999 and 2002.

The coefficients of determination (r^2), slopes for the lines of best fit (m), and intercepts are shown for the regression between log concentration (pg g^{-1} wet weight) and distance (km) from the smelter in the 1999 control (n=33) and 2002 (n=43) samples. Individual regressions were run for both 1999 and 2002 individuals, and a significant decline with distance, if detected, is indicated in the r^2 column. An ANCOVA model indicated whether the slopes (m) were significantly different between the 1999 and 2002 individuals (distance*year interaction term), and significance in this model, if detected, is indicted beside the 2002 slope (m). Significance is reported at the 95% confidence level: *($p<0.05$); **($p<0.01$); ***($p<0.001$).

	1999			2002		
PCB Congener	r^2	m	Intercept	r^2	m	Intercept
$\sum PCB_3$						
16-32	0.088*	0.018	1.36	0.003	0.003	1.67
31-28	0.025	0.009	1.96	0.006	0.004	2.24
22	0.019*	0.022*	1.13	0.000	-0.001	1.59
33-20-53	0.013*	-0.017	1.98	0.002	0.002	1.82
18	0.067	0.020	1.91	0.078*	0.022	1.77
15-17	0.033	0.008	2.05	0.000	-0.001	2.08
54-29	0.016	-0.005	2.39	0.009	-0.004	2.46
26	0.15*	0.015	0.92	0.115*	-0.025*	2.32
$\sum PCB_4$						
52	0.008	-0.004	1.60	0.047	-0.010	1.95
45	0.016*	-0.019*	1.96	0.067	0.014	1.58
43	0.003	-0.007	1.77	0.000	0.001	1.78
48-47	0.033	0.011	1.64	0.001	-0.002	1.87
44	0.002	-0.003	1.60	0.013	-0.006	1.81
59-42	0.000	-0.000	1.24	0.031	-0.010	1.43
40	0.065	-0.011	1.66	0.001	-0.006	1.72
74	0.016	-0.004	2.08	0.017	-0.007	1.99
70-76-98	0.007	-0.007	2.31	0.002	0.003	2.11
66	0.079	-0.019	1.68	0.001	-0.003	1.59

PCB Congener	1999			2002		
	r^2	m	Intercept	r^2	m	Intercept
$\sum PCB_4$						
91-55	0.107*	0.016	1.24	0.019	-0.006	1.52
56-60	0.087*	0.026	1.73	0.001	-0.002	2.07
87-81	0.000	0.001	1.49	0.049	-0.012	1.68
$\sum PCB_5$						
92	0.045	0.011	1.43	0.002	0.003	1.51
84	0.045	-0.011	1.69	0.015	-0.007	1.52
101	0.051	0.014	1.76	0.278***	-0.035**	2.32
99	0.017	0.005	1.96	0.096*	-0.017*	2.15
97	0.007	-0.005	1.48	0.021	-0.012	1.34
85	0.011	-0.007	1.74	0.000	-0.001	1.79
110	0.000	0.001	1.62	0.02	-0.006	1.79
82	0.013	-0.006	1.42	0.005	-0.005	1.50
118	0.008	0.004	2.23	0.048	-0.011	2.43
114-134-131	0.001	0.002	1.70	0.013	-0.006	1.90
153-105-132	0.001	0.001	2.64	0.074*	-0.011	2.90
$\sum PCB_6$						
136	0.035	-0.012	1.92	0.026	-0.010	2.14
151	0.014	-0.008	1.34	0.004	-0.004	1.35
135-144	0.009	-0.005	1.55	0.005	-0.006	1.52
149	0.006	0.005	1.43	0.006	-0.004	1.69
133	0.004	0.004	1.82	0.108*	-0.012	2.26
146	0.089*	-0.012	2.02	0.044	-0.014	2.13
141-179	0.000	-0.001	1.29	0.02	0.007	1.26
130-176	0.053	-0.01	1.46	0.037	-0.001	1.28
138-163	0.014	0.005	2.22	0.136*	-0.017*	2.67
158	0.002	0.003	1.51	0.000	-0.010	1.43
128	0.001	-0.003	1.15	0.012	-0.007	1.39
167	0.005	0.003	1.82	0.05	-0.014	2.02
157-200	0.006	0.006	2.27	0.011	0.008	2.38

PCB Congener	1999			2002		
	r^2	m	Intercept	r^2	m	Intercept
$\sum PCB_7$						
187-182	0.05	0.015	1.27	0.234**	-0.028**	2.06
178	0.203*	0.019	0.29	0.313*	-0.038**	2.05
174	0.000	0.000	1.26	0.001	-0.002	1.35
177	0.001	0.001	1.46	0.078*	-0.013	1.77
171-156-202	0.012	-0.007	1.67	0.006	-0.005	1.81
180	0.041	-0.007	2.42	0.052	-0.013	2.49
170-190	0.001	-0.005	1.85	0.040	-0.018	2.13
193	0.003	0.003	1.31	0.138*	-0.025*	1.67
191	0.010	0.005	1.56	0.097*	-0.013	0.96
$\sum PCB_8$						
201	0.00	0.001	1.85	0.207**	-0.026**	2.37
203-196	0.000	0.001	1.27	0.007	-0.004	1.59
195-208	0.001	0.002	0.20	0.026	-0.010	1.56
194	0.001	-0.002	1.44	0.024	-0.010	1.60
$\sum PCB_9$						
206	0.021	0.006	0.32	0.052	-0.015	1.65
207	0.039	-0.011	1.56	0.001	0.002	1.57
$\sum PCB_{10}$						
209	0.003	0.003	0.31	0.03	-0.011	1.69

Appendix 3.3 Percentage of PCB homologues and select congeners above detection limits (DL).

Sample Size for 1999 (n=33) and 2002 (n=43).

PCB	1999 % above DL	2002 % above DL
PCB Homologue		
Mono +		
Dichlorinated	18.18	13.95
Trichlorinated	27.27	41.86
Tetrachloinated	30.30	46.51
Pentachlorinated	81.82	88.37
Hexachlorianted	78.79	95.35
Heptachlroinated	72.73	76.74
Octachlorinated	12.12	44.19
Nonachlorinated	18.18	55.81
Decachlorinated	18.18	51.16
PCB Congeners		
31-28	27.00	58.00
52	18.18	27.91
74	90.91	79.07
99	90.91	86.05
101	60.61	51.16
118	84.85	88.37
133	9.09	16.28
138-163	81.82	90.70
153-132-105	100	97.67
177	48.48	60.47
180	93.94	79.07
187-182	60.61	72.09
193	36.36	48.84
201	87.88	90.70
209	18.18	51.16

Appendix 3.4 Percentage of organochlorine pesticides above detection limits (DL).

Sample Size for 1999 (n=33) and 2002 (n=43).

Organochlorine Pesticide	1999 % above DL	2002 % above DL
1,3-DCB	0	0
1,4-DCB	0	0
1,2-DCB	0	0
1,3,5-TCB	0	0
1,2,4-TCB	0	0
1,2,3-TCB	0	0
1,2,3,4-TTCB	0	0
PECB	39.39	41.86
α-HCH	72.73	58.14
HCB	100	100
γ-HCH (lindane)	30.30	25.58
Heptachlor	0	13.95
Aldrin	3	0
Heptachlor Epoxide	30.30	46.51
g-Chlordane	15.15	44.19
a-Endosulfan	54.55	41.86
a-Chlordane	9.09	34.88
Dieldrin	75.76	76.74
ppDDE	39.39	55.81
Endrin	3.03	2.32
b-Endosulfan	12.12	13.95
ppDDD	3.03	13.95
opDDT	0	4.65
ppDDT	21.21	41.86
Methoxychlor	0	13.95

Appendix 3.5 Summary of coplanar PCB and PCDD/F concentrations in deer samples expressed in pg/g wet weight (n=12).

deer age:	1	3	1	2	1	2	2	1	1	4	1	1
dist (km):	11.5	3.65	3.04	4.09	4.15	4.96	4.17	7.55	11.6	16.43	23.41	31.16
Sampe ID:	577	573	519	560	571	502	501	569	555	570	509	566
PCDD/Fs												
2378-TCDF	6.31	1.83	0.37	0.74	0.29	0.00	0.24	0.00	0.67	0.63	0.00	0.11
12378-PeCDF	0.24	7.97	1.24	2.67	0.40	0.39	0.19	0.00	2.23	2.84	0.27	0.18
23478-PeCDF	0.55	11.95	1.85	3.83	0.78	0.81	0.57	0.00	3.44	4.02	0.36	0.32
123478-HxCDF	0.44	10.09	1.52	3.05	0.58	0.50	0.29	0.00	3.18	3.43	0.34	0.25
123678-HxCDF	0.46	9.72	1.48	3.36	0.49	0.45	0.18	0.00	3.04	3.42	0.35	0.17
123789-HxCDF	1.23	13.83	1.89	4.26	0.65	0.44	0.24	0.00	4.46	4.46	0.47	0.22
234678-HxCDF	0.22	14.62	2.09	4.12	0.49	0.34	0.17	0.00	4.04	4.21	0.41	0.19
1234678-HpCDF	0.57	9.53	1.50	3.65	0.39	0.57	0.19	0.16	3.75	3.56	0.40	0.22
1234789-HpCDF	0.34	12.31	2.03	4.27	0.38	0.35	0.16	0.00	4.28	3.90	0.39	0.12
OCDF	1.66	35.14	4.78	10.04	0.95	0.82	0.29	0.47	15.39	12.10	1.02	0.27
∑PCDFs	12.03	126.99	18.74	39.97	5.38	4.67	2.52	0.64	44.47	42.56	4.00	2.05
2378-TCDD	0.00	1.62	0.34	0.48	0.30	0.18	0.21	0.00	0.39	0.56	0.12	0.00
12378-PeCDD	0.30	9.68	1.62	3.16	0.56	0.48	0.38	0.00	3.08	3.26	0.33	0.00
123478-HxCDD	0.89	10.93	2.18	4.10	1.03	0.93	0.82	0.75	3.68	3.73	0.79	0.72
123678-HxCDD	0.20	10.48	1.45	3.26	0.36	0.47	0.31	0.00	3.28	3.58	0.00	0.00
123789-HxCDD	0.29	13.03	2.07	3.95	0.49	0.36	0.32	0.00	3.51	3.65	0.38	0.25
1234678-HpCDD	0.62	11.38	1.45	3.81	0.77	0.56	0.26	0.30	4.39	3.98	0.49	0.37
OCDD	1.95	24.12	3.82	9.71	1.99	1.91	1.37	0.90	9.83	8.73	1.39	0.95
∑PCDDs	4.25	81.24	12.94	28.47	5.50	4.87	3.68	1.94	28.16	27.47	3.50	2.30
∑PCDD/Fs	16.28	208.23	31.68	68.45	10.88	9.54	6.20	2.58	72.63	70.04	7.50	4.35
no-PCBs												
PCB 77	8.52	6.00	11.72	9.31	4.45	20.48	7.05	3.20	5.55	4.65	2.86	5.47
PCB 126	6.64	120.75	20.22	18.63	10.93	37.07	21.53	4.77	7.93	7.62	3.62	6.30
PCB 169	2.31	25.03	13.42	1.92	1.41	18.85	3.90	1.31	1.55	1.48	1.28	1.27
∑no-PCBs	17.47	151.78	45.36	29.86	16.79	76.40	32.48	9.28	15.03	13.75	7.76	13.04
∑PCB+PCDD/F	33.75	360.01	77.04	98.31	27.67	85.94	38.68	11.86	87.66	83.79	15.26	17.39

Appendix 3.6 Summary of coplanar PCB and PCDD/F concentrations in deer samples expressed in pg TEQ/g (n=12).

	deer age:	1	3	1	2	1	2	2	1	4	1	1	1
	dist (km):	11.5	3.65	3.04	4.09	4.15	4.96	4.17	31.16	16.43	23.41	7.55	11.6
	Sample ID	577	573	519	560	571	502	501	566	570	509	569	555
PCDD/Fs	**TEFa**												
2378-TCDF	0.1	0.63	0.18	0.04	0.07	0.03	0.00	0.02	0.01	0.06	0.00	0.00	0.07
12378-PeCDF	0.05	0.01	0.40	0.06	0.13	0.02	0.02	0.01	0.01	0.14	0.01	0.00	0.11
23478-PeCDF	0.5	0.27	5.97	0.93	1.92	0.39	0.41	0.29	0.16	2.01	0.18	0.00	1.72
123478-HxCDF	0.1	0.04	1.01	0.15	0.31	0.06	0.05	0.03	0.02	0.34	0.03	0.00	0.32
123678-HxCDF	0.1	0.05	0.97	0.15	0.34	0.05	0.05	0.02	0.02	0.34	0.03	0.00	0.30
123789-HxCDF	0.1	0.12	1.38	0.19	0.43	0.07	0.04	0.02	0.02	0.45	0.05	0.00	0.45
234678-HxCDF	0.1	0.02	1.46	0.21	0.41	0.05	0.03	0.02	0.02	0.42	0.04	0.00	0.40
1234678-HpCDF	0.01	0.01	0.10	0.01	0.04	0.00	0.01	0.00	0.00	0.04	0.00	0.00	0.04
1234789-HpCDF	0.01	0.00	0.12	0.02	0.04	0.00	0.00	0.00	0.00	0.04	0.00	0.00	0.04
OCDF	0.0001	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
∑PCDFs		**1.16**	**11.60**	**1.76**	**3.68**	**0.67**	**0.61**	**0.41**	**0.26**	**3.84**	**0.36**	**0.00**	**3.45**
2378-TCDD	1	0.00	1.62	0.34	0.48	0.30	0.18	0.21	0.00	0.56	0.12	0.00	0.39
12378-PeCDD	1	0.30	9.68	1.62	3.16	0.56	0.48	0.38	0.00	3.26	0.33	0.00	3.08
123478-HxCDD	0.1	0.09	1.09	0.22	0.41	0.10	0.09	0.08	0.07	0.37	0.08	0.07	0.37
123678-HxCDD	0.1	0.02	1.05	0.15	0.33	0.04	0.05	0.03	0.00	0.36	0.00	0.00	0.33
123789-HxCDD	0.1	0.03	1.30	0.21	0.39	0.05	0.04	0.03	0.02	0.36	0.04	0.00	0.35
1234678-HpCDD	0.01	0.01	0.11	0.01	0.04	0.01	0.01	0.00	0.00	0.04	0.00	0.00	0.04
OCDD	0.0001	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
∑PCDDs		**0.45**	**14.86**	**2.55**	**4.81**	**1.06**	**0.84**	**0.74**	**0.10**	**4.95**	**0.56**	**0.08**	**4.57**
∑PCDD/Fs		**1.61**	**26.46**	**4.31**	**8.49**	**1.72**	**1.45**	**1.15**	**0.37**	**8.79**	**0.92**	**0.08**	**8.02**
no-PCBs													
PCB 77	0.0001	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PCB 126	0.1	0.66	12.08	2.02	1.86	1.09	3.71	2.15	0.63	0.76	0.36	0.48	0.79
PCB 169	0.01	0.02	0.25	0.13	0.02	0.01	0.19	0.04	0.01	0.01	0.01	0.01	0.02
∑no-PCBs		**0.69**	**12.33**	**2.16**	**1.88**	**1.11**	**3.90**	**2.19**	**0.64**	**0.78**	**0.38**	**0.49**	**0.81**
∑PCB+PCDD/F		**2.30**	**38.79**	**6.46**	**10.38**	**2.83**	**5.34**	**3.34**	**1.01**	**9.57**	**1.30**	**0.57**	**8.83**

Les chevreuils contaminés par Magnola

Denis Dufresne
ASBESTOS

Les inquiétudes de la Coalition pour un Magnola propre étaient fondées: les rejets liés à la production de magnésium chez Métallurgie Magnola, de 2001 à 2002, ont entraîné une accumulation de polluants organiques persistants chez les chevreuils de la région.

Telle est la conclusion de l'étude du biologiste et éco-toxicologue Jules Blais et de l'étudiante Cecilia Tolley, de l'Université d'Ottawa, réalisée avec la collaboration de chasseurs, de la Coalition et de Daniel Green (Société pour vaincre la pollution).

«En comparant les données de 1999 et de 2002, nous avons vu une augmentation des concentrations de dioxines, furanes, BPC (biphényles polychlorés) et chlorobenzènes chez les chevreuils», confirme le Dr Blais, qui a présenté, hier soir à Asbestos, les grandes lignes de son étude devant une trentaine de citoyens.

«Cela nous donne une bonne indication que la contamination vient de Magnola», a-t-il livré.

«Nous considérons toutefois que les concentrations ne dépassent pas les normes de l'Organisation mondiale de la santé (OMS), mais on pourrait dire qu'on a commencé à approcher de la limite», ajoute le chercheur.

Ce dernier reconnaît qu'il est difficile d'évaluer l'impact réel sur la population environnante, mais précise qu'une personne aurait pu prendre trois repas par semaine de viande provenant du chevreuil ayant affiché les plus fortes concentrations, sans dépasser la limite pour sa santé».

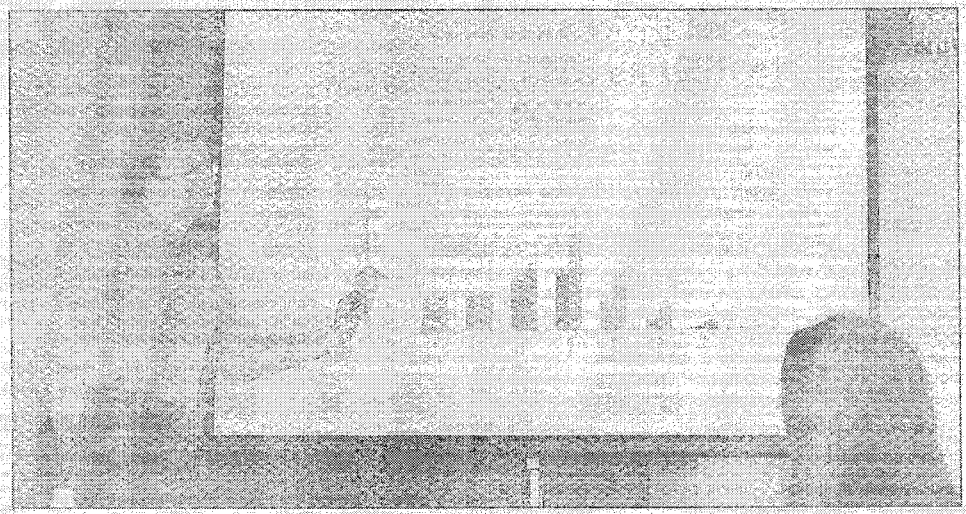
Fait à signaler, Métallurgie Magnola n'a fonctionné qu'à 16 pour cent de sa capacité en 2001 et à 43 pour cent en 2002.

De plus, a souligné le Dr Blais, «les émissions étaient en général moins élevées que prévu».

L'usine a fermé ses portes au printemps 2003, après à peine deux ans et demi d'exploitation, en raison de la baisse du prix du magnésium et de la concurrence chinoise.

Les dioxines et furanes, qui font partie des organochlorés, sont bannis par la Convention de Stockholm, dont le Canada est signataire.

Ces produits pénètrent progressivement dans l'environnement et s'accumulent dans la chaîne alimentaire. Ils peuvent affecter les systèmes endocrinien, reproducteur, nerveux et immunitaire des êtres vivants.



Le Dr Jules Blais, biologiste et éco-toxicologue à l'Université d'Ottawa, a dévoilé hier soir à Asbestos les conclusions d'une étude sur l'impact des rejets d'organochlorés de Métallurgie Magnola pour la population de chevreuils de la région.

le.com, Jessica Garneau

Appendix 3.7 La Tribune article June 8, 2005. Section A5 « Les chevreuils contaminés par Magnola. »

Dans un rayon de 30 km

Le Dr Jules Blais a supervisé la cueillette des échantillons de muscles, de graisses et de dents de dizaines de chevreuils mâles abattus durant ces trois années par les chasseurs, dans un rayon de 30 kilomètres autour de l'usine.

Il a précisé qu'on avait mesuré «jusqu'au double» de contaminants chez les chevreuils entre 1999 et 2002 et que la concentration des polluants augmente à mesure que l'on se rapproche de l'usine.

«Si nous parlons des BPC [contenus dans un rayon de cinq kilomètres et moins de l'usine, c'est de trois à quatre fois plus», a-t-il dit en réponse à la question d'un citoyen.

La situation aurait-elle pu être pire si Magnola avait poursuivi ses opérations jusqu'à aujourd'hui? Là-dessus, le Dr Blais s'est limité à dire que «l'étude représente la situation en 2002».

«Il existe une possibilité qu'avec des émissions qui auraient continué, ces concentrations auraient augmenté», a-t-il ajouté toutefois.

Un autre citoyen a demandé si la population s'était inquiétée pour rien.

À cela, le Dr Blais a répondu que «la concentration d'organochlorés a augmenté après seulement deux ans et on commence à approcher des limites pour la consommation humaine».

Pour ce qui est de l'impact sur les vaches laitières, nombreuses dans la région, le chercheur indique que «si nous voyons cette tendance-là chez les chevreuils (la bio-accumulation via la consommation de végétaux), la situation ne serait pas différente avec les vaches».

Arlene Fillion, une productrice de brebis laitières de Saint-Rémi-de-Tingwick, à 15 kilomètres de l'usine, a toutefois mentionné que des tests effectués sur son cheptel par l'Union des producteurs agricoles «avaient démontré des traces de BPC dans le lait en 2001, alors qu'il n'y en avait pas en 1999».

Victoire des citoyens

La présidente de la Coalition pour un Magnola propre, Lisette Anfousse, considère pour sa part que les résultats de l'étude constituent «une victoire pour les citoyens».

Elle rappelle que le projet d'usine avait été autorisé par décret gouvernemental malgré un rapport du Bureau d'audiences publiques sur l'environnement à l'effet que les activités de Magnola pouvaient nuire à la santé des citoyens.

«Je trouve cela concluant et si jamais il est question d'une réouverture, il faudrait alors qu'ils apportent des changements majeurs. Si la production avait continué jusqu'en 2005, peut-être serions nous rendus au seuil de risque», juge-t-elle.

Le représentant de Magnola sur place, Bernard Hinse, a expliqué pour sa part que la compagnie entend étudier dans le détail les conclusions de l'étude.

«C'est trop tôt pour donner une opinion, bien qu'il y ait certaines contradictions avec d'autres études déjà effectuées», a-t-il dit.

Appendix 3.7 La Tribune article June 8, 2005. Section A5 « Les chevreuils contaminés par Magnola. »


LE DEVOIR, LE JEUDI 9 JUIN 2005

A 3

ACTUALITÉS

Appendix 3.8 Le Devoir article June 9, 2005. Section A3 « Dioxines, furannes et BPC au menu des chevreuils. »

Dioxines, furannes et BPC au menu des chevreuils

Les taux d'organochlorés dans la chair des animaux vivant près de l'ancienne usine Magnola ont quadruplé en deux ans

En général, les gouvernements exigent un suivi environnemental des projets industriels en examinant l'évolution de leurs rejets dans l'eau, le sol et l'air. Des écologistes, citoyens et chercheurs viennent de démontrer qu'un suivi des contaminants sur des animaux permet de voir beaucoup plus clairement l'infiltration et l'accumulation des toxiques dans la chaîne alimentaire. Un modèle à généraliser, disent les chercheurs.

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Une étude inédite réalisée par des chercheurs de l'Université d'Ottawa démontre que le taux d'organochlorés, y compris des dioxines, des furannes et des BPC, a augmenté de trois à quatre fois dans la chair des cerfs de Virginie abattus à la chasse dans un rayon de cinq kilomètres de l'usine Magnola, aujourd'hui fermée.

Ces résultats, qui n'indiquent pas que la santé des chasseurs-consommateurs ait été mise en péril, sont cependant d'autant plus spectaculaires que cette augmentation de contaminants aussi dangereux et aussi persistants a été constatée après seulement deux ans d'exploitation de l'usine, dont le taux de fonctionnement s'était limité à l'époque entre 16 et 43 % de sa capacité maximale en raison de problèmes de rodage.

Cette étude, lancée à l'initiative du groupe environnemental SVP et de la Coalition pour un Magnola propre, a été réalisée par Cecilia Tolley, une candidate à la maîtrise, et par son professeur, Jules Blais, du département de biologie de l'Université d'Ottawa. Les tests, a expliqué hier M. Blais au *Devoir*, ont été effectués par les laboratoires d'Environnement Canada.

L'intérêt majeur de cette étude réside dans le fait qu'elle permet de comparer la situation des cerfs de Virginie — nos «chevreuils» en langage populaire — avant la construction de l'usine, soit ceux qui ont été abattus localement à l'automne 1999, avec ceux abattus par la suite. Le Bureau d'audiences publiques sur l'environnement (BAPE) avait avisé Québec des impacts potentiels sur la santé publique des éventuels rejets de l'usine.

Si on ne tient aucunement compte de la distance à laquelle vivaient les chevreuils abattus autour de l'usine Magnola, située dans la région d'Asbestos et de Danville, les concentrations d'organochlorés des cerfs de cette région a augmenté en moyenne de deux fois environ, expliquait hier le biologiste Blais. Mais si on se restreint aux concentrations moyennes relevées aux abords de l'usine, soit dans un rayon de cinq kilomètres, les concentrations de dioxines, furannes, BPC et chlorobenzènes ont augmenté *«de trois à quatre fois»* en deux ans, ont découvert les chercheurs.

Ce phénomène est d'autant plus intéressant sur le plan scientifique, explique-t-on, que les photos ou les instantanés que les gouvernements prennent par des prélèvements dans les rejets atmosphériques ou aquatiques d'une usine de cette ampleur ne sont pas toujours éloquents parce qu'ils portent sur des concentrations infimes, parfois indécelables. L'intérêt de suivre les animaux qui vivent autour d'une telle usine réside dans le fait qu'ils mangent les plantes sur lesquelles les contaminants s'abattent en quantités infimes et que le phénomène de la bioaccumulation met en relief l'effet cumulatif de concentrations infimes, parfois indécelables mais réelles.

«Il faudrait toujours exiger un portrait de ce genre avant la construction d'équipements industriels majeurs, a expliqué Jules Blais, *car les résultats qu'on obtient peuvent alors être attribués à la nouvelle usine, ce qu'on ne peut pas faire quand on n'a pas le portrait de la situation antérieure à la construction. Des études de ce genre font aussi apparaître plus clairement les effets à long terme de la présence de contaminants et les risques pour la population.»*

Par exemple, a précisé le professeur de biologie, le taux le plus élevé d'organochlorés relevé dans un cerf aurait néanmoins autorisé qu'on en mange trois fois par semaine sans dépasser les seuils de sécurité recommandés par l'Organisation mondiale de la santé. Cependant, a-t-il aussitôt ajouté, ces taux commençaient à se rapprocher des seuils de sécurité, et il est plausible que si l'usine avait atteint son plein rendement et tourné pendant dix ou quinze ans, le portrait de la situation aurait alors pu devenir plus préoccupant.

Alors que les BPC sont réputés pour affecter notamment le développement neurophysiologique des enfants, réduire la mémoire et engendrer des déficiences du système neurologique, les dioxines et furannes sont des composés cancérigènes et mutagènes, de surcroît capables d'induire d'importants impacts neurotoxicologiques, a résumé le chercheur.

Le Devoir

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