Lead Levels and Sources of Exposure in Migratory Game Birds After the Implementation of Lead-free shot in Canada

Amy L. Stevenson
Natural Resource Sciences
McGill University, Montreal
November 2002

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements of the Master of Science degree in Wildlife Biology

Your file Votre référence
ISBN: 0-612-88306-X
Our file Notre référence
ISBN: 0-612-88306-X

Abstract

In Canada, regulations against the use of lead (Pb) shot for waterfowl hunting were first established in the early 1990s with the creation of a few non-toxic shot zones, and culminated with a national ban in 1997. Prior to establishment of the first non-toxic shot zones in Canada, a nation-wide survey of Pb accumulation in wing bones of young-of-the-year (YY) dabbling and diving ducks determined the incidence of elevated Pb exposure in different parts of the country (Scheuhammer & Dickson, 1996). The objective of the present study was to determine the incidence of elevated Pb accumulation in the same species several years after the national ban on Pb shot; to survey waterfowl hunters to determine approximate levels of compliance with the Pb shot ban; and to use stable Pb isotope analysis to help determine the relative importance of different sources of Pb exposure.

Wing bones from 721 YY black, mallard, and ring necked ducks, and 579 YY woodcock from selected zones in Ontario, Quebec, BC, and the Maritimes, Canada were analyzed for Pb using flame atomic absorption spectrometry. Samples containing >0.50 μg/g Pb were further analyzed for stable Pb isotopes using ICP-MS. Average bone Pb concentrations in dabbling ducks (Mallards [*Anas platyrhyncos*] and American black ducks [*Anas rubripes*] combined) decreased significantly between 1990 and 2000 (11.32 μg/g vs. 4.78 μg/g, respectively). Ring necked ducks (*Aythya collaris*) similarly showed a significant decrease in mean bone Pb concentrations, from 28.04 μg/g to 10.13 μg/g. These data are compatible with our anonymous hunter survey results, which indicate a high compliance (>80%) with the Pb shot ban. On the other hand, American woodcock (*Scolopax minor*), an upland game species not affected by the Pb shot ban, showed no decrease in mean bone Pb concentration between 1996 and 2001 (18.7 μg/g vs. 21.2 μg/g, respectively).

Stable Pb isotope analysis of dabblers with elevated levels of bone Pb in Southern Ontario showed $Pb^{206:207}$ signatures (1.19 ± 0.04) consistent with Pb shot pellets continuing to be the major source of high Pb exposure, indicating that some Pb shot may still be available for ingestion despite the ban on the use of Pb shot for waterfowl hunting. Dabblers with high Pb exposure in BC and Rouyn-Noranda area showed $Pb^{206:207}$ signatures (1.15) different from those for southern Ontario, and more characteristic of the signature for leaded gasoline typically used in Canada prior to the early 1980s (1.14-1.16). Young of the year woodcocks showed a mean $Pb^{206:207}$ signature of 1.18 ± 0.02, consistent with exposure to lead shot pellets, or possibly a mixture of Pb sources.

Résume

En au Canada, des règlements contre l'utilisation du projectile de plomb (Pb) pour la chasse d'oiseaux aquatiques ont été établis la première fois au début des années 1990s avec la création de quelques zones non-toxiques de projectile, et culminés avec une interdiction nationale en 1997. Avant l'établissement des premières zones non-toxiques de projectile au Canada, un aperçu répandu par tout le pays d'accumulation de Pb dans des os d'aile de l'jeune-de-année (YY) mouillant et des canards de plongée a déterminé l'incidence de l'exposition du Pb élevée dans différentes parties du pays (Scheuhammer et Dickson, 1996). L'objectif de la présente étude était de déterminer l'incidence de l'accumulation élevée de Pb dans la même espèce plusieurs années après que l'interdiction nationale du projectile de Pb; pour examiner des chasseurs d'oiseaux aquatiques pour déterminer les niveaux approximatifs de la conformité à l'interdiction de projectile de Pb; et pour employer l'analyse isotopique stable de Pb pour aider à déterminer l'importance relative de différentes sources d'exposition du Pb.

Envolez-vous les os de 721 YY noirs, de mallard, et sonnez les canards étranglés, et le woodcock de 579 YY des zones choisies Ontario, Québec, BC, et le Maritimes, Canada ont été analysés le Pb en utilisant la spectrométrie par absorption atomique de flamme. Des échantillons contenant > 0,50 Pb de µg/g ont été encore analysés les isotopes stables de Pb en utilisant ICPMS. Concentrations moyennes en Pb d'os dans les canards barbotants (Mallards [*Anas platyrhyncos*] et canards noirs américains [*Anas rubripes*] combinés) diminuées sensiblement entre 1990 et 2000 (11.32 µg/g contre. 4.78 µg/g, respectivement). Les canards étranglés d'anneau (*Aythya collaris*) ont pareillement montré une diminution significative des concentrations moyennes en Pb d'os, de 28.04 µg/g à 10.13 µg/g. Ces données sont compatibles avec nos résultats anonymes d'enquête de chasseur, qui indiquent une conformité élevée (> 80%) avec l'interdiction de projectile de Pb. D'autre part, le woodcock américain (*Scolopax minor*), une espèce de jeu de montagne non affectée par le Pb a tiré l'interdiction, non montrée aucune diminution de concentration moyenne en Pb d'os entre 1996 et 2001 (18.7 µg/g contre. 21.2 µg/g, respectivement).

L'analyse isotopique stable de Pb des amateurs avec les niveaux élevés du Pb d'os dans Ontario méridional a montré les signatures $Pb^{206:207}$ (1.19± 0.04) conformées aux granules de projectile de Pb continuant à être la source principale d'exposition du Pb élevée, indiquant qu'un certain projectile de Pb peut encore être disponible pour l'ingestion en dépit de l'interdiction de l'utilisation du Pb tirée pour la chasse d'oiseaux aquatiques. Les amateurs avec l'exposition du Pb élevée dedans BC et la région de Rouyn-Noranda ont montré les signatures $Pb^{206:207}$ (1.15) différentes de ceux pour Ontario méridional, et plus caractéristiques de la signature pour l'essence plombée typiquement utilisée au Canada avant le début des années 80 (1.13-1.16). Les jeunes des woodcocks d'année ont montré une signature $Pb^{206:207}$ moyenne du 1.18 ± 0.02, conformée à l'exposition aux granules de projectile de fil, ou probablement à un mélange des sources de Pb.

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Acknowledgements

We all 'stand on the shoulders of giants', to quote Isaac Newton, and I would like to thank them all.

I would first like to thank my advisors, Drs. Tony Schuehammer and Laurie Chan for their wealth of wisdom and experience. Without their financial and moral support I would not have been able to complete this thesis, or even begin it. I would like to thank Dr. Rodger Titman for keeping me on track with the ecological issues, and for reminding me of how it all fits together.

I would like to thank Ewa Neugebauer, Angela Clark, Della Bond and Margaret Antler for their patience, support and help with the laboratory instruments and analysis of results. Without their knowledge and support this thesis would not be here today, and there would be large scraps of metal, glass and chemicals strewn around the lab after I had beaten the instrument with a hammer.

I give a big thank you to Jen Holloway, for being the 'big sister' and showing me around, providing advice and friendship and for helping, along with Becky Perkins to dissect all those stinky wings.

I would like to thank everyone in the Department of Natural Resource Sciences and CINE for moral support, advice and friendship. In particular, Caroline Begg, Chris Blanar, Janna Carefoot, Kim Fernie, and Josee Rouseau. I will always remember my time at McGill with fondness and a smile.

I thank my parents for a lifetime of support. They have always encouraged me to be and do what I wanted. They have had undying patience, and never ending words of encouragement. I hope that one day I may be able to repay them for their kindness, love and support.

Lastly, but far from least I would like to thank my husband, Matt. Who made dinners AND did the dishes, cleaned the house, took care of Azul, paid the bills, edited my papers, listened to me cry, whine, rant and rave. Who helped me through late nights and long days and threatened to lock me in the office until this thesis was done. Without his love, support, friendship and threats this thesis would not exist.

Chapter 1 Introduction

1.1 Introduction

Lead (Pb) is a toxic metal whose physical and chemical characteristics have made it one of the most extensively used metals in the world. The environmental and human health consequences of the production and dissemination of Pb products and the emissions resulting from mining and smelting of Pb-bearing ores have been the subject of much scientific and public interest. Although progress has been made in reducing emissions and exposure to humans and the environment, Pb continues to be a concern for environmental and human health, especially in developing countries (Sangster et al. 2000).

In addition to its harmful effects on humans, Pb has also inflicted damage on some species of wildlife. Pb poisoning in waterfowl was recorded as early as 1874 (Phillips and Lincoln 1930), when large die-offs of waterfowl "unfit for human consumption" due to Pb poisoning were found in Texas and North Carolina. Other die-offs of waterfowl have been documented across North America. Most of the large die-offs occurred during the late fall and early winter months, immediately after the close of hunting season (Bellrose 1959). Annual losses attributed to Pb poisoning were conservatively estimated to be 2-3 % of the fall population of waterfowl in North America before regulations against the use of Pb shot came into effect (Bellrose 1959).

Ingestion of Pb shot pellets deposited into the environment has been the primary source of exposure in waterfowl (Sanderson and Bellrose 1986, Scheuhammer and Dickson 1996). However, other sources of Pb exposure have been also documented. The ingestion of food or sediment contaminated by mining and smelting activities (Chupp and Dalke 1964; Beyer et al. 1985; Blus et al. 1991) and the introduction of Pb into the environment from industrial processes such as battery manufacturing, secondary Pb smelting and the use of leaded gasoline (Kisseberth et al. 1984; Birdsall et al. 1986; Grue et al. 1986; Bache et al. 1991) are all potentially important sources of environmental Pb contamination and Pb exposure in wildlife.

Due to the toxic consequences of Pb deposited into the environment, regulations have been put in place to reduce Pb exposure to humans and wildlife. Restrictions on the use of Pb in gasoline and the ban on the use of Pb shot for hunting migratory game birds are prime examples of such restrictions, which have reduced the amount of Pb released into the environment; however, Pb poisoning persists and continues to be of concern to both human health experts and wildlife managers. Although identifying the source of Pb exposure can be problematic, relatively recent advances in analytical instrumentation have provided additional tools to aid in this endeavor.

Lead has four stable isotopes (204, 206, 207 and 208), whose ratios vary as a function of its geologic/geographic origin. These differences allow for the identification of characteristic Pb isotope signatures, which can be used in many cases to identify or eliminate specific sources of Pb exposure.

Stable Pb isotope analysis has been used to discriminate between sources of Pb in the environment (Sturges and Barrie 1987, 1989; Smith et al.. 1990; Scheuhammer and Templeton 1998; Steding et al.. 2000). While there are a variety of methods and instrumentation available to analyze stable Pb isotopes, inductively coupled plasma mass spectrometry (ICP-MS) provides an accurate and time and cost effective method (Delves and Campbell 1988).

The purpose of this thesis is to attempt to determine the sources of elevated Pb exposure currently important for migratory game birds in Canada using ICP-MS, and to determine the level of hunter compliance with the national ban on the use of Pb shot for hunting waterfowl. Hunter compliance will be assessed in two independent ways: 1) comparison of bone Pb concentrations in YY ducks before and after the ban on Pb shot; and 2) an anonymous survey of migratory bird permit holders.

1.2 Hypotheses

The study was designed to test the following hypotheses:

1. Lead shot exposure is the primary source of Pb contamination in waterfowl.

2. Lead shot exposure is the primary source of Pb contamination in the American woodcock (an upland game bird).

3. Exposure of waterfowl to Pb shot, and hence bone-Pb accumulation, has been reduced since the 1999 national ban on hunting waterfowl with Pb shot.

4. Hunters are complying with the 1999 national ban on Pb shot for hunting waterfowl.

Chapter 2 Literature Review

2.1 A Brief History of Lead

Known as *plumbum* in Latin, from which the chemical symbol "Pb" is derived, Pb was one of the seven metals of antiquity. Lead is one of the most useful industrial metals. Because of its softness and lack of luster, it has found little application in weaponry or jewelry. However, Pb's resistance to corrosion and formability made it a valuable metal extensively used in plumbing, building, and ship construction as well as for stationary. Its density and malleability made it attractive as plummets and sinkers for fishing nets and lines. A low melting point enabled its use as solder in tin food cans, and its atomic configuration enabled large amounts of Pb to be added to silicate glass where it functioned as an opacifier or a colorant. Several compounds of Pb are brilliantly colored and have been valued as pigments since Paleolithic times (Nriagu, 1983).

The first known Pb object was a statue found in Catal Huyuk, Turkey, dating from 6500 BC. Lead was used for medicinal purposes as far back as 4000 BC where galena (lead sulfide; PbS) was commonly used as an eye salve in Egypt and Asia. The first significant production of Pb was in 3000 BC and the Romans began smelting in 500-300 BC. Around 400 BC, Pb was often prescribed by physicians as a contraceptive, as well as for treating intestinal obstructions. The utilization of Pb was so extensive during Roman times that it is often referred to as "Roman metal." The pervasive use of Pb by Rome likely led to considerable contamination of food and drink, leading to a theory that the decline of Roman civilization was partly due to epidemic levels of Pb poisoning (Nriagu 1983).

In more modern times, Pb has been used for a number of different purposes including: an antiknock agent in gasoline, X-ray and radiation shielding, waterproofing materials, noise and vibration barriers. It has been manufactured into various consumer products such as optics, electronics and computers, sports equipment, shotgun pellets, fishing weights and batteries (Nriagu 1983).

The high toxicity of Pb to humans and wildlife has led to a number of restrictions and bans on its use in many of these products. In spite of the restrictions, Pb continues to be a persistent environmental contaminant.

2.2 Lead Toxicity

Lead has been listed as a pollutant of concern to the United States Environmental Protection Agency's (EPA) Great Waters Program due to its persistence in the environment, potential to bio-accumulate, and toxicity to humans and wildlife (USEPA 1994).

Exposure to Pb, even at low levels, may cause a variety of physiological, developmental and behavioral impairments. Main pathways for Pb exposure are through inhalation of contaminated air or dust and ingestion of contaminated dust, soil, water or food.

In humans acute exposure to high levels of Pb may cause brain damage, kidney damage, and gastrointestinal distress. Chronic exposure to Pb results in toxic effects on the blood, central nervous system (CNS), blood pressure, kidneys, and Vitamin D metabolism. Children are particularly sensitive to the chronic effects of Pb, with slowed cognitive development, and reduced growth. Reproductive effects, such as decreased sperm count in men and spontaneous abortions in women, have been associated with high Pb exposure. The developing fetus is at particular risk from maternal Pb exposure, resulting in low birth weight and slowed postnatal neurobehavioral development (ATSDR 1997).

Perhaps the best-known effect of Pb exposure is its inhibition of heme synthesis. Lead interferes with the critical phases of the dehydration of aminolevulinic acid and the incorporation of iron into the protoporphyrin molecule. This results in a decrease in heme production. Because heme is essential for cellular oxidation, deficiencies have far-reaching effects (Marcus 2001).

Toxicity of Pb in wildlife depends on a variety of factors such as species, sex, diet, dose, and pathway and duration of exposure. Gastrointestinal absorption and retention of soluble Pb salts from the diet in mammals is 10% or less of the administered dose (Van Barneveld and Van den Hamer 1985). Because of its high affinity of mineralized tissue, the skeleton accumulates approximately 95% of the total body burden of Pb in mammals (Stowe et al. 1973).

Normal background levels of Pb in tissues of adult bird species living in relatively uncontaminated areas are 2-15 µg/g in bone, 1-10 µg/g in kidney, and 0.3 – 5.0 µg/g in liver (dry weight; Kendall and Scanlon 1981; Custer et al. 1984). Bone Pb concentrations of 19 captive and wild Canada geese (*Branta canadenis*) known not to be suffering from Pb poisoning, ranged from 2-11 µg/g (Szymcazk and Adrian 1978). A number of various species of marsh birds in Texas were examined for lead shot ingestion. Birds with no shot found in the gizzard had an average bone Pb concentration of 5.47 µg/g (Hall and Fisher 1985).

In general, sub lethal effects of Pb poisoning include lowered reproductive success, impairment of the central and peripheral nervous systems, increased kidney weight, renal intranuclear inclusion bodies, altered mitochondrial structure and function and depressed δ aminolevulinic acid dehydratase (ALAD) activity in the blood, liver and kidney (Hutton 1980; Scheuhammer 1987). Immune function also can be impaired by Pb as shown both by dysfunction of specific components of the immune system and increased susceptibility to bacterial and viral pathogens in animals sub-lethally poisoned with Pb (Kendall et al. 1996). Lowered food intake, greenish diarrhea, impaired locomotion, drooping wings, decreased body weight and food impaction in the proventriculus are common symptoms of Pb poisoned birds (Koh and Harper, 1988).

Acute lethal Pb exposure may result in a quick death where the bird appears to be in relatively good body condition, while chronic exposure may result in a prolonged lingering death where birds are often found in a very emaciated condition (Sanderson and Bellrose, 1986).

Female birds, especially during reproduction, tend to accumulate Pb at greater rates than males. Bone tissue of reproductively active female Ringed turtle doves

(*Streptopelia risoria*) (Kendell and Scanlon 1981) and feral pigeons (*Columba livia*) (Janiga and Zemberyova 1998) revealed a greater accumulation of Pb than that of males. Reproductively active females (layers) accumulated 4-5 times more Pb in bone than non-laying females because Pb accumulation in bone is enhanced as a result of calcium (Ca) mobilization from bone during eggshell formation (Finley and Dieter 1978). This was consistent with Taylor (1970) who suggested that increased mobility of skeletal Ca needed for eggshell formation during reproduction may be a factor in the increased accumulation of Pb. Levels of dietary Ca and protein can affect the accumulation and toxicity of Pb from exposure via ingestion (Kendall et al. 1996). Van Barneveld and Van den Hamer (1985) found that feeding rats a Ca deprived diet for 2 weeks prior to an oral dose of Pb increased absorption of Pb by more than 100%. The increased uptake and retention of Pb observed under conditions of deficient or marginal Ca intake results in the production of toxic effects at much lower levels of dietary Pb than would normally occur (Scheuhammer 1987).

Differences in response to Pb exposure results from a combination of dose and chemical form of Pb ingested, the length of retention of Pb in the digestive system, species-specific factors that affect Pb absorption, components in diet (carnivorous or herbivorous) that may affect Pb dissolution and absorption, and the environmental condition in which the bird must respond (Kendall et al. 1996). For example, Vyas et al. (2001) found that cowbirds dosed with one 7.5 mm Pb shot absorbed sufficient Pb to compromise their survival, even though retention rates were minimal. On the other hand, male adult quails dosed with 10 size 8 Pb pellets per week showed no significant effect on body weight or food intake but did result in increased mortality (Damron and Wilson 1975). Japanese quail fed a diet containing 10 μg/g Pb showed a significant reduction in plasma Ca and egg production in hens while 200 μg/g Pb was required to obtain similar results in chickens (Edens and Garlich 1983). Additionally, breeding American kestrels (*Falco sparverius*) fed 50 μg/g Pb had no adverse effects with respect to egg laying, incubation, fertility or eggshell thickness (Pattee 1984) and breeding Ringed turtle doves treated with 100 μg/g Pb in their drinking water had a tendency to produce smaller number of fledglings than the control group (Kendall and Scanlon 1981).

2.3 Sources of Lead in the Environment

Metallic Pb is rarely found in nature, but Pb ores have been exploited by humans for over 6500 years. Total global output of Pb from mining is estimated to be 260 x 10^6 metric tons, most of which was extracted within the last two centuries (Nriagu 1998). Current (2000) annual global production of Pb from mining is about 3.1 x 10^6 tons of which approximately 73% is produced in the western world (Europe and the Americas) (ILZSG 2000). The U.S. is one of the major producers of refined Pb, representing 23% of world production. Current Pb mine production has decreased in the U.S by about 9% from 1999 to 2000. Nearly 77% of current Pb production in North America was derived through recycling, predominately Pb-acid batteries.

Sources of Pb exposure to wildlife can be classified into three main categories: 1) Pb 'artifacts' (Pb shot and fishing sinkers); 2) mining and smelting wastes; and 3) "urban Pb," primarily from past gasoline combustion.

2.3.1 Lead Shot

Numerous studies have attributed the main source of Pb exposure in waterfowl and upland game birds to the ingestion of spent Pb shot pellets (Stendell et al. 1980; Anderson et al. 1987; Kennedy and Nadeau 1993; Scheuhammer and Norris 1995; Kendall et al. 1996; Wilson et al. 1998). The availability of Pb shot to waterfowl utilizing a particular body of water is determined by a number of factors such as shooting intensity, firmness of the lake bottom, size of the shot pellets deposited, depth of water and duration of ice cover (Bellrose 1959).

In Canada, an estimated 9.5 million game birds (48% upland game, 50% waterfowl, and 2% other migratory game birds) are harvested annually by licensed hunters and First Nations people (CWS, unpubl. data). On average approximately six shots are fired for every duck harvested (USFWS 1986). Prior to the ban on Pb shot, each shell load used in waterfowl hunting contained about 35 grams of Pb, while upland game loads generally contained 28 grams of Pb. Currently, it is no longer legal to use Pb shot for waterfowl hunting, but it is still used for hunting upland game birds. Prior to any ban on Pb shot, approximately 1,812 tons of Pb was deposited annually into the Canadian environment from hunting with shotguns. Assuming a high compliance rate, the 1999 national ban on Pb shot should have reduced the amount of Pb deposited into the Canadian environment by approximately 1,000 tons Pb/yr. Small mammal hunting and recreational trap and skeet shooting ranges annually contribute about 532 and 260 tons of Pb, respectively (CWS, unpublished data).

Pellets deposited in marshes, fields and on lake bottoms, are mistaken by foraging birds for food or grit. Ingested pellets often remain in the gizzard, especially in waterfowl, and are slowly ground down, allowing Pb to be absorbed. Lead deposited into the environment in the form of pellets that were not ingested by wildlife was formerly believed to be inert. However, Jorgensen and Willems (1987) determined that Pb pellets deposited on soil are slowly oxidized making the Pb bio-available to soil invertebrates and plants. Within 6-13 years, 5- 17% of metallic Pb had been transformed. Stansley and Roscoe (1996) found Pb concentrations in the soil of a trap and skeet range to be 1000 times higher than in soil of a control field after Pb pellets were removed. Elevated tissue Pb concentrations and depressed ALAD activities in small mammals and frogs captured at the site indicated that some of this Pb was bio-available. This agrees with the findings of Manninen and Tanskanen (1993) who reported Pb concentrations as high as 54,000 μg/g in the humus layer from a shooting range. Castrale (1989) documented an increase in soil shot densities from a pre-hunting season density of 3,228 shot/ha to a post-hunting season density of 24,665 shot/ha on 14 agricultural fields located in 9 state managed wildlife areas throughout Indiana. Daury et al. (1992) estimated shot densities for 4 heavily hunted marshes on Prince Edward Island (PEI) and in Nova Scotia, Canada. Shot densities for the PEI marshes increased from 29,000 –49,000 shot/ha in 1988 to 87,000 – 90,000 shot/ha in 1989 and Nova Scotia marshes showed an increase in shot densities from 23,000-32,000 shot/ha in 1988 to 31,000-45,000 shot/ha in 1989 (Daury et al. 1992). Various efforts to reduce the exposure of waterfowl to Pb shot pellets have been made by wildlife managers. For example, Peters and Afton (1993) found that tilling of the soil reduced the amount of pellets available in the top 10 cm of soil by 95%.

However, Jorgensen and Willems (1987) found that transformation of Pb from metallic to molecular compounds was accelerated when pellets were mixed with the upper soil layers by plowing.

Acidic soils tend to increase the rate of biodegradation of Pb shot pellets (Jorgensen and Willems 1987). Ma (1989) reported elevated Pb concentrations in both herbivorous and carnivorous small mammals on an abandoned shooting range with acidic soils (pH 3.9). Significant concentrations of filterable Pb in a slightly acidic marsh (pH6.3) located in the shot fall zone of a shooting range suggests that Pb may be mobilized at lower pH (Stansley et al. 1992).

Environmental exposure of some birds, particularly waterfowl, to Pb was correlated to hunting intensity. Bellrose (1959), Szymczak and Adrian (1978) and Stendell (1980) found that incidences of Pb ingestion and Pb poisoning increased soon after hunting season, in areas of high hunting activity. Scheuhammer and Dickson (1996) compared patterns of hunting with levels of Pb contamination in 'young of the year' waterfowl across Canada. Areas of higher hunting activity tended to contain higher frequencies of birds with elevated (≥ 10 μg/g) levels of Pb in their bones.

In an attempt to decrease the concentration of Pb in waterfowl habitat, regulations in the U.S. and Canada banning the use of Pb shot for hunting migratory birds began with the implementation of nontoxic shot zones in 1976 and 1991, respectively. These zones were selected in areas where 5% (U.S.) or 10% (Canada) and greater of the population sampled had more then one Pb pellet in the gizzard or tissue levels above allowable background levels. A nationwide ban on the use of Pb for hunting waterfowl in all areas was fully implemented in 1991 in the U.S and 1999 in Canada (USFWS 1999; Scheuhammer and Norris 1995). However, Pb shot is still used for hunting upland game birds and small mammals as well as for trap and skeet ranges.

2.3.2 Mine Wastes and Smelter Emissions

Mining of metals has occurred for centuries, the Romans being the first to fully develop and expand the practical uses and mining of Pb (Blaskett and Boxall 1990). Lead is deposited into the air, soil and water from mining and smelting of lead, gold, silver, nickel and copper/zinc. In 1999, 3,495.3 tons of Pb was emitted as 'on-site' releases into the Canadian environment, 10% (337.42 t) of which can be attributed to mining and smelting industries (NPRI 1999). 'On-site' releases consist of discharges within the boundaries of the facility, which include: (1) air: stack/point, storage/handling, and non-point releases, (2) surface waters: through leaks, spills and discharges, (3) land: landfill, land treatment, spills, and leaks and (4) deep-well underground injection (NPRI 1999).

Contamination of the environment from mines and smelting activities tends to be fairly localized. However, wind and watershed topography carry a proportion of the pollutants away from the main source. A study by the Geological Survey of Canada found that Pb and other heavy metals demonstrated a 'bullseye' pattern of soil contamination, where highest concentrations of Pb were found closest to the source of emission, with concentrations declining as distance from the source increased (McMartin and Henderson 2000).

A well-known case of Pb mobility due to watershed topography is the Coeur d'Alene River Basin in Idaho. Mining and smelting activities in Northern Idaho began in the 1880's after deposits of gold, silver, Pb and other metals were discovered. Average monthly emissions of Pb from the main smelter stack were estimated at 8 to 12 metric tons from 1955 to 1973 (Burrow et al... 1981). As late as 1973, daily discharges of metals into the South Fork River included 4,400 kg of zinc, 245 kg of Pb and 57 kg or arsenic (Rabe and Flaherty 1974). Approximately 75 million tons of metal-enriched sediments associated with mining activities have been deposited downstream into the lake bed of Coeur d'Alene and on to the flood plain, associated wetlands and lateral lakes of the Coeur d'Alene river (Horowitz et al. 1993). Lead concentrations in the sediment of many lateral lakes were found to be 3,000-5,000 μg/g (dw)(Campbell et al. 1999).

Commercial mining in the Big River watershed of southeastern Missouri began in the early 1700's (Ekberg 1982) and continued through 1972. The river drains what was formerly the leading Pb mining district in the world (Kramer 1976). Tailings totaling over 200 metric tons, rich in heavy metals, have accumulated in the Big River watershed. These metals enter the watershed via erosion and seepage from tailing ponds. A dam breach in 1977 at one of the tailing ponds washed 38,230 m^3 of tailings directly into the river (Novak and Hasselwander 1980). Lead levels measured in fish after the spill exceeded the maximum safe level of Pb in the diet of adult humans as recommended by the World Health Organization (Niethammer et al. 1985).

Large floods may also contribute to moving Pb through the environment. In 1908, contaminated soil from mining activities was swept 100 miles downstream to be deposited behind the Milltown Dam on the Clark Fork in Montana. High levels of Pb and other heavy metals are found behind the dam in wetland and upland soils, and surface and ground water (Pascoe et al. 1994).

2.3.3 Urban Lead

The general term 'urban lead' was born with the industrial revolution and encompasses a variety of industrial sources of Pb such as battery manufacturing, municipal incinerators, recycling outlets, steel production, and electronic and textile productions. Geo-chemical information analyzed by the National Academy of Sciences (1980) reported natural particulate Pb levels to be less than 0.0005 $\mu g/m^3$, in contrast some urban environments have reported to have Pb concentrations as high as 6 $\mu g/m^3$ (USEPA 1979). The primary source of urban Pb prior to the 1980s in the U.S and Canada was emissions of Pb in gasoline (Sturges and Barrie 1987).

In 1993, an estimated 70,000 tons of Pb, primarily in the form of tetra-ethyl Pb (TEL) were added to gasoline worldwide as an antiknock agent for combustion engines (Thomas 1995). TEL Pb undergoes transformation *in vivo* to neurotoxic trialkyl metabolites as well as further conversion to inorganic Pb (USEPA 1986). Thus, chronic and acute exposure to TEL results in damage to the central nervous system, which can manifest as nausea, vomiting, convulsions, delirium, fever, memory loss, and possibly death (USEPA, EC 1999).

Prior to restrictions on the use of Pb as an anti-knock agent in gasoline for combustion engines, the majority of Pb compounds (90%) found in the atmosphere resulted from the combustion of leaded gasoline (USEPA 1986). In 1984, total Pb emissions in the US, as a result of the combustion of leaded gasoline, was estimated to be 34, 881 tons/year (USEPA 1986). These Pb emissions occur from the exhaust pipe as inorganic Pb bromine chlorine (PbBrCl) particles. During the lifetime of the vehicle approximately 35% of the Pb emitted in vehicle exhaust are small particles (<0.25 μm), and approximately 40% is emitted as larger particles (> 10 μm). The remaining Pb is deposited on the engine and exhaust system. The Pb particles in these emissions can enter the food chain by being deposited in soil, water and on plants.

When airborne, small particles can remain suspended in the atmosphere for 7-30 days and travel thousand of miles from their original source. A small portion of the Pb emitted from the combustion of leaded gasoline is in the form of organolead vapors (i.e. lead alkyls) such as tetra-ethyl lead (TEL). TEL vapors are produced mainly from the manufacture, transport and handling of leaded gasoline. The vapors are photo-reactive and they contribute less than 10% of the total Pb present in the atmosphere.

In 1975 the U.S. Environmental Protection Agency (EPA) began phasing out the use of Pb in gasoline and 20 years later, in December 1995 the use of Pb in gasoline was banned for non-commercial vehicles. Over a 20-year period (1980–1999), Pb emissions from vehicles dropped 95%. Airplanes are now the primary source of transportation emissions and contribute 13% of total Pb emissions to the air. This leaves industrial manufacturers and processors responsible for most of the current Pb emissions (USEPA 1999).

In Canada, leaded gasoline was prohibited in December 1990 under the Canadian Environmental Protection Act. Gas regulations limited the concentration of Pb in gasoline to 500 μg/dl in cars and trucks and 3000 μg/dl for farm equipment, boats and heavy-duty trucks (EC 1990).

Solid waste incineration and combustion of waste oil are principal contributors of Pb emissions from stationary sources, contributing approximately 1,200 tons of aerosol Pb emissions in 1984 (EPA 1986). Approximately 10% of the 160 million metric tons of combustible refuse is incinerated annually in the United States (Wallgren 1987). A variety of toxins, including Pb, are found in the suspended particulates and emitted gases from refuse incinerators. Lead emissions vary in concentration depending on materials burned and quantity of such materials. Lead chromate used for the yellow and red color inks in magazines and newspaper inserts are a notable source of Pb (EU 2002). Discarded batteries are an additional source of Pb, Hg, Cd and Zn especially when incinerated (Bergstrom 1986). Bache et al. (1991) found that Pb concentrations in the soil downwind of a municipal refuse incinerator were highest (29.8 μg/g, dw.) within 100 meters of the facility.

Lead is used to manufacture end-use products such as batteries, ammunition, covering for power cables, construction materials and electrical components. Lead-acid battery production accounts for approximately 87% of Pb consumption in the U.S. and is currently the predominant source of scrap Pb for recycling. In 2000, an estimated 1.04 million metric tons of Pb was contained in Pb-acid batteries (USGS 2000). The Pb from these manufactured products can enter the environment through aerosol emissions and Pb particulates from stockpiled batteries and scrap. Kisseberth et al. (1984) found 7 cows with signs of Pb toxicosis on an Illinois farm located near a battery Pb reclamation plant. Small mammals on the Ayers Sand Prairie Nature Preserve near the same plant showed elevated levels of Pb up to 400 meters from the plant.

In Canada during 1999, chemical industries released 2.3 x 10^6 kg of Pb, of which 99% was released on land. Metal manufacturers and product industries released 9.4 x 10^5 kg, textile/electronic/plastic manufacturers released 2.9 x 10^4 kg, coal combustion and transportation industries released 2.4 x 10^3 kg and miscellaneous industrial processes contributed 1.9 x 10^5 kg of Pb into the environment (NPRI 1999).

2.4 Lead Exposure in Game Birds

The primary source of Pb exposure in some wild bird species, especially waterfowl, is from the ingestion of spent Pb shot pellets (Sanderson and Bellrose 1986; Scheuhammer and Dickson 1998). However, environmental Pb contamination from mining wastes (Blus et al. 1991; Chupp and Dalke 1964; and Roberts et al. 1978) and urban industries such as waste incinerators, and leaded gasoline (Chow 1970) may be a greater concern for other, non-hunted birds.

Waterfowl and upland game birds ingest Pb shot pellets deposited into the environment, mistaking the pellets for food or grit. The Pb is then slowly metabolized causing lethal and sub-lethal effects. Pb shot ingestion rates are typically determined through examination of gizzards collected from hunters during the fall and early winter. The percentage of waterfowl that ingest shot depends upon hunting pressure, feeding habits and varying habitats. Since these factors can change from year to year and region to region, so can ingestion rates. In a compilation of data from numerous studies, that includes various duck species, Sanderson and Bellrose (1986) reported an overall presence of shot in 8.9% of 171,697 duck gizzards analyzed. However, ducks that have ingested Pb shot are 1.65 times more likely to be harvested by hunters, and when this bias is taken into account, the Pb ingestion rate for waterfowl populations is reduced to approximately 5.4%. Species that feed most actively on the bottom, such as Ring-necked ducks (*Aytha collaris*) and Lesser scaup (*Aythya affinis*), have the highest rate of shot ingestion (Bellrose 1959). When extrapolated to a North American duck 'meta-population' of over 60 million individuals, it can be appreciated that many millions of waterfowl ingest spent shot pellets every year.

Approximately 1,500 waterfowl, most of which were Lesser scaup, died during an outbreak of Pb poisoning at Rice lake, Illinois in the spring of 1972. Anderson (1975) found that 75% of the scaups examined had at least one Pb pellet and 36% had more than 10 pellets in their gizzard; and found that the number of pellets in the gizzard was significantly related to body weight, and Pb concentrations in the kidney and wing bone. A positive correlation between Pb concentrations in the liver and concentrations of Pb in wing bones was also noted.

Hall and Fisher (1985) documented a correlation between feeding habits, bill length and ingestion of Pb shot of 14 different species of marsh birds. Birds with a bill length >6cm were exposed to approximately 63% of the available Pb shot and therefore at greater risk of ingesting spent Pb pellets.

Ingestion of Pb pellets in upland game birds has not been studied as comprehensively as in waterfowl. Nonetheless, shot ingestion has been documented in a number of upland species, including Ring-necked pheasants (*Phasianus colchicus*), Northern bobwhite (*Colinus virginianus*), Wild turkey (*Meleagris gallopavo*), Hungarian partridge (*Perdix perdix*), Sandhill crane (*Gurs canadensis*) and Mourning doves

(*Zenaida macroura*) (Kendall et al. 1996). Ingestion rates in Mourning doves varied depending on time of year and area. A review of Mourning dove studies indicated a ingestion rate of between 0.2 and 6.4% (Kendall et al. 1996).

Scheuhammer et al. (1999) investigated the Pb accumulation in American woodcocks in Eastern Canada. Concentrations of Pb found in the wing bones of approximately 1,600 American woodcocks were surprisingly high, with 51.5% of adults and 29% of YYs having elevated Pb levels (>20 μg/g dw). Lead shot ingestion by woodcock has not been reported yet it is suspected, due to feeding habits. Woodcocks probe the soil with their long flexible bill in search of earthworms and other invertebrates (Keppie and Whiting 1994). Exposure from contaminated soils via ingestion of contaminated earthworms may also be a source of Pb exposure for woodcocks.

Lead exposure to wild birds and mammals from mine wastes and smelters has been of concern in certain locations. Documentation of Pb poisoning in Tundra swans, Whistling swans, Canada geese and 8 species of ducks in the Coeur d'Alene River system of northern Idaho was reported by Chupp and Dalke (1964) and Blus et al. (1991). Elevated Pb concentrations and evidence of clinical plumbism was identified in small mammals from an abandoned metalliferous mine in Wales (Roberts et al... 1978). Downwind of two zinc smelters in Pennsylvania, Pb concentrations in soils were measured at 2,700 μg/g and concentrations of Pb in the carcasses (external fur removed) of short-tailed shrews (*Blarina brevicauda*) were found to be 109 μg/g dw (Beyer et al. 1985). Niethammer et al. (1985) found elevated concentrations of Pb in northern water snakes, bullfrogs, muskrats and green-backed herons that were collected downstream from the Pb mining district of the Big River in southeastern Missouri. In addition, bank swallows nesting in a tailings pile were reported to have Pb levels significantly higher than northern rough-winged swallows, which did not nest in the tailings. Lead uptake in rooted plants, algae and invertebrates downstream of the mines on the Big River were reported by Schmitt and Finger (1982). Scheuhammer and Dickson (1996) found elevated Pb concentrations in 42% of young dabbling ducks shot in the vicinity of 50 different mine sites in Ontario and Quebec.

A number of studies have examined the effects of Pb from leaded gasoline combustion on plants, soils and wildlife near highways. In general, the concentrations of Pb in soil, vegetation, invertebrates, and small mammals correlated with the traffic density and distance from highways (Getz et al. 1977; Goldsmith and Scanlon 1977; Williamson and Evans 1972; Chow 1970). Lead concentrations in plants and invertebrates near heavily traveled roads were found to be elevated as high as 1,180 μg/g in vegetation and 700 μg/g in invertebrates (Williamson and Evans 1972) yet did not appear to be magnified through trophic levels (Williamson and Evans 1972). Invertebrates with the highest concentrations of Pb were those that possess calcareous exoskeletons and soil decomposers (Williamson and Evans 1972). Grue et al. (1986) found that European starlings nesting within highway roadside verges had elevated Pb concentrations and depressed ALAD levels in comparison to controls, yet this did not seem to affect the reproductive success or survival of these birds.

Lead poisoning of 40 Holstein cows from a battery Pb reclamation plant adjacent to the farm in northwestern Illinois lead to an investigation by the neighboring Ayers Sand Prairie Nature Preserve. Soil, vegetation and small mammals were reported with elevated Pb concentrations increasing with proximity to the reclamation plant (Kisseberth et al. 1984). Scheuhammer and Templeton (1998) found that juvenile herring gulls (*Larus argentatus*) from the Canadian Great Lakes had Pb bone concentrations ranging from 4.1-23.8 μg/g dw, and had Pb isotope ratios matching those for leaded gasoline compounds in Canada (^{206}Pb:^{207}Pb = 1.13–1.16; Sturges and Barrie 1989).

2.5 Stable Lead Isotopes

Lead can be characterized and its origin can often be identified by its stable isotopic composition. Lead isotope abundance varies between ore bodies of different age and location as a result of the different accumulation of radiogenic Pb. Radiogenic Pb is the product of radioactive decay of uranium and thorium that has been associated with the Pb during geological time. The relative abundance of radiogenic isotopes depends on how long the Pb and its radioactive parents were together in the mantle and crust before the Pb was segregated (Brown 1962). Lead has 13 isotopes of which four are stable:

non-radiogenic Pb^{204}, Pb^{206} derived from U^{238}, Pb^{207} derived from U^{235} and Pb^{208} derived from Th^{232}. There are six combinations of the ratios, all of which are useful in determining the geologic origin of Pb, however the $Pb^{206:207}$ ratio is most commonly used and accepted in environmental studies (Brown 1962; Scheuhammer and Templeton, 1998). While isotope ratios from different sources may not be unique, regional ratios may be characteristic and sufficiently stable to determine a source (Sangster et al. 2000). Lead from the oldest geological formations will have the lowest $Pb^{206:207}$ ratios. For the Canadian Precambrian ore sources, 206/207 ratios range between 0.93-1.08. Newer (non-Precambrian) Pb sources have higher ratios, typically ranging from 1.15 to 1.22. The Mississippi Valley ores have the highest North American $Pb^{206:207}$ ratios, ranging from 1.27 to 1.37 (Brown 1962 and Sangster et al. 2000).

Stable Pb isotopes have been used to help determine sources of air pollution. Maring et al. (1987) used stable Pb isotopes to determine the geological origin of atmospheric Pb emission sources in the Mediterranean region. Sturges and Barrie (1987) differentiated US and Canadian sources of airborne Pb in the Great Lakes region. US $Pb^{206:207}$ ratios showed an average 'marker' of 1.217 ± 0.009, while Canadian $Pb^{206:207}$ emission sources showed a lower 'marker' average of 1.151 ± 0.006. Flegal et al. (1989) used stable Pb isotopes to determine the origin of industrial Pb contamination in the Great Lakes. $Pb^{206:207}$ ratios with a range of 1.147-1.160 in the western and central basins of Lake Ontario corresponded to the $Pb^{206:207}$ ratios for aerosols in the Toronto metropolitan area ($Pb^{206:207} = 1.151 \pm 0.010$ (Sturges and Barrie 1987), typical of the ratio for leaded gasoline in Canada.

Smith et al. (1990) used stable Pb isotopes to find evidence of anthropogenic Pb contamination in Alaskan sea otters. $Pb^{206:207}$ ratios of pre-industrial otter teeth (~1.16) and contemporary teeth (~1.21) were compared and it was observed that the source of Pb exposure in Alaskan otters has undergone a pronounced change through time. Exposure in pre-industrial otters was found to be from natural geologic sources found in the Aleutian Arch, while contemporary otters are exposed to Pb originating mainly from Asian and Canadian industrial sources. Stable Pb isotopes were used to verify that the San Francisco Bay estuary system contained past industrial Pb emissions (Steding et al.

2000). In Turin, Italy, Pb isotopes were used to identify the source of Pb exposure in humans (Facchetti et al. 1984). Lead from leaded gasoline accounted for approximately 5 μg/dl of blood Pb levels for persons living in Turin and 3 μg/dl for persons living outside the city. Scheuhammer and Templeton (1998) used $Pb^{206:207}$ ratios to determine sources of Pb exposure in wild birds. They reported the range of $Pb^{206:207}$ ratios in tissues of waterfowl and raptors that had elevated Pb exposure were similar to that for Pb shot pellets whereas juvenile herring gulls, a species that only infrequently, if ever, ingest Pb shot, exhibited a mean isotope ratio (1.137) characteristic of Pb from gasoline used in Canada.

Inductively Coupled Plasma Mass Spectrophotometer (ICP-MS)

Isotopic analysis of metals is commonly performed using inductively coupled plasma mass spectrometry (ICP-MS). The instrument originated in the 1960's with the advent of a technique called inductively coupled plasma-atomic emission spectrometry (ICP-AES). The unique feature of this instrument was the use of an atmospheric pressure argon inductively coupled plasma (ICP) for sample atomization and atomic excitation (Taylor 2001). By coupling the ICP with a mass spectrometer, Houk et al. (1980) discovered that measuring ion currents produced higher signal–to-background ratios, yielding significantly higher analytical sensitivity, which resulted in improved detection limits.

Inductively coupled plasmas are formed by coupling energy produced by a radio frequency (RF) generator to the plasma support gas with an electromagnetic field. The field is produced by applying an RF power to a 3 cm diameter copper load coil. The coil is positioned around a quartz torch assembly, which configures and confines the plasma. The plasma is initiated by the spark of a Tesla coil providing a few "seed" electrons to the flow of argon. The plasma is sustained by the continued collision of these seed electrons with neutral argon gas atoms. The collisions produce more electrons, which in turn collide with additional neutral argon gas atoms. This cascading effect creates and sustains the plasma (Taylor 2001).

An aqueous solution is converted to an aerosol by a nebulization process and transported to the plasma by an argon gas stream. In the plasma the analyte elements are atomized, followed immediately by ionization. The composition of the ion population in the plasma is proportional to the concentration of the analyte in the original sample solution. The ions are then filtered through the center of four cylindrical charged rods. The ion species of interest are allowed to pass through while other ion species are detained. The magnitude of the ion beam of interest is then measured via a multiplier-type detector.

ICP-MS has the ability to determine the isotopic composition of sample materials more efficiently and cost effectively then thermal ionization mass spectrometry (TIMS). However, quadropole mass analyzers are specifically designed for scanning of relatively large mass ranges and are therefore not suited for highly precise and accurate isotope ratio measurements (Begley and Sharp 1997). Instrumental and sample matrix-related biases have been observed (Gilson et al. 1988; Ross and Hieftje 1991). Yet these biases can be dealt with by appropriate tuning (Begley and Sharp 1997; Ting and Janghorbani 1988), performing corrections based upon separately analyzed control samples (Hinners et al. 1987), and by simultaneous measurement of ^{205}Tl:^{203}Tl in each sample (Ketterer et al. 1991). Using these techniques, quadropole analyzers are capable of providing sufficient accuracy to be useful in many isotope ratio studies. The precision of isotope ratio measurements made by quadropole ICP-MS approaches 0.1% RSD for isotopes of similar abundance (Ince et al. 1993). For isotope ratios involving an isotope of low abundance, such as ^{204}Pb, a precision of 0.2 to 1.0 % RSD is typical (Ketterer 1992). The accuracy and precision of the ^{207}Pb:^{206}Pb ratio measurement for NIST SRM 981 Natural Lead is generally 0.2-0.3%.

Chapter 3 Determination of Lead Sources in Exposed Migratory Game Birds by Stable Lead Isotope Analysis

3.1 Introduction

The problem of Pb poisoning in wild birds, such as swans (WDFW 2001) and raptors (Meretsky 2000), persists despite a national ban in the U.S and Canada on the use of Pb shot for hunting waterfowl. It has been accepted and documented that ingestion of Pb shot pellets was the primary source of elevated Pb exposure in waterfowl prior to current broad regulations in the U.S. and Canada prohibiting the use of Pb shot for waterfowl hunting (Sanderson and Bellrose 1986; Scheuhammer and Templeton 1998). Scheuhammer and Dickson (1996) examined the spatial relationship between Pb exposure and waterfowl hunting intensities across Canada. As would be expected, areas with heavy hunting intensity tended to have high concentrations of Pb in the wing bones of hunter shot waterfowl. However, wings with elevated levels of Pb were collected from areas with low/moderate hunting intensities. Median bone Pb concentrations for young of the year (YY) dabblers from eastern Canada was 5.7 μg/g, consistent with median bone Pb in immature mallards collected in 1972-73 from the US Atlantic flyway, reported to be 5.5 μg/g (Stendell et al. 1979).

With national bans on the use of Pb shot for hunting migratory game birds in both the U.S. and Canada, exposure to Pb shot is expected to have declined, but exposure to other environmental sources of Pb, such as Pb from mining and smelting wastes, Pb using industries, or Pb from past gasoline combustion, may not have declined significantly. Differentiating other sources of Pb exposure among game birds can be difficult, yet identification of such sources would be helpful in estimating the relative importance of different sources of Pb exposure in different species of game birds.

The use of ICP-MS stable Pb isotope analysis has proven useful in differentiating sources of Pb in a number of environmental studies (Maring et al. 1987; Flegal et al. 1989; Sturges and Barrie 1989; Scheuhammer and Templeton 1998; Steding et al. 2000). This study examines changes in mean bone Pb concentrations of different migratory game birds since the national ban on Pb shot. ICP-MS stable Pb isotope analysis is then utilized in an attempt to determine the relative importance of different sources of Pb in exposed birds.

3.2 Methods

3.2.1 Sample Collection

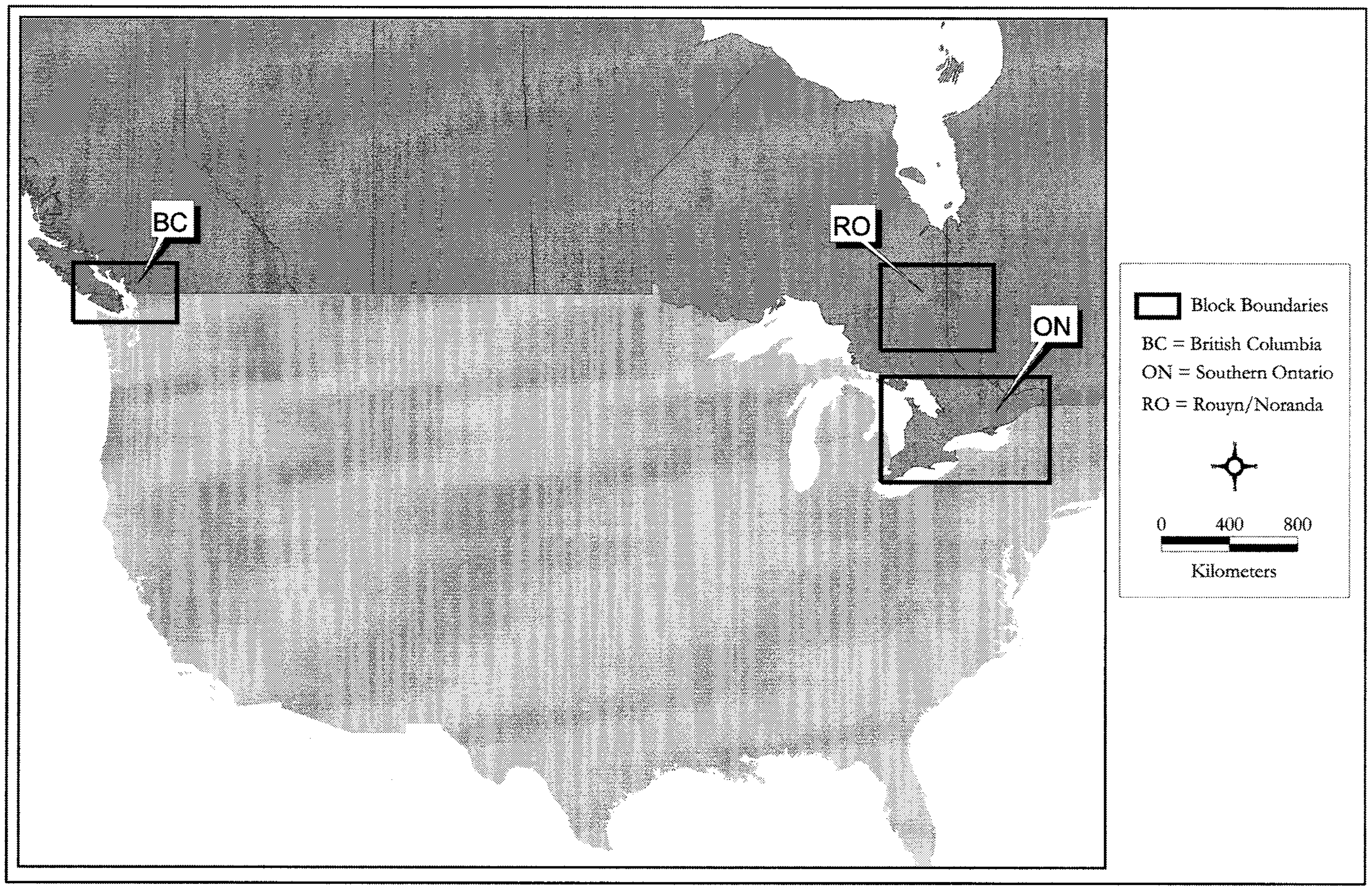
Wings from across Canada were voluntarily submitted by hunters to the Canadian Wildlife Service (CWS) as part of the National Harvest Survey during the 2000 hunting season. Information on hunting location and date the bird was shot was included with each wing. Wings from three species of waterfowl [Mallard (*Anas platyrhynchos*), American black duck (*Anas rubripes*, Ring-necked duck (*Aythya collaris*)] and one upland game bird [American woodcock (*Scolopax minor)*] were collected. Only young of the year (YY) wings were collected to ensure that Pb exposure was obtained from Canadian sources between hatching and migration.

Waterfowl wings were selected from three study blocks (Figure 3.1). Dickson and Scheuhammer (1993) characterized 4 categories of hunting intensities: light (0-199 hunter-days/year), moderate (200-499 hunter-days/year), heavy (500-1999 hunter-days/year) and very heavy (2000 or more hunter-days/year), which were used to help derive the current study blocks. The British Columbia (BC) study block encompasses one of the first Canadian 'non-toxic shot zones' implemented in the early 1990s, and includes heavy hunting intensities. The Southern Ontario (ON) study block is characterized by a mixture of hunting intensities ranging from 'low' to 'very heavy.' Lastly, the Rouyn-Noranda (RO) study block includes areas characterized by numerous non-ferrous metal mining and smelting activities in north-eastern Ontario and north-western Quebec. This block has low or moderate hunting pressure.

Adult and YY woodcock wings were collected from Ontario (ON), Quebec (PQ), New Brunswick (NB) and Nova Scotia (NS). Woodcocks are generally not utilized in the CWS national harvest survey, therefore information on hunting location was not available for many wings.

Each wing was identified by species, aged and sexed by experienced biologists and then placed in individual plastic bags, given an ID number and sealed. The samples were shipped to the National Wildlife Research Center (NWRC) in Hull, Quebec where they were stored at -80° C until analyzed.

Figure 3.1 Map of three study blocks



3.2.2 Sample Preparation

The radius of each wing was excised and extraneous tissue removed. Each bone was placed into a pre-weighed, acid washed glass test tube, stored at -80° C overnight and freeze-dried for 48 hours. All wings showing damage were discarded to ensure against the possibility of contamination. Each sample was weighed again to obtain a dry weight and % moisture of the bone was calculated. Samples were re-hydrated with 0.5 ml of Nanopure water and digested overnight in 3.5 ml of trace metals grade Nitric acid (HNO_3:FISHER Sci. 70%: Nepean, Ontario). The digests were heated to 100° C for a minimum of 4 hours to complete digestion. Cooled samples were brought to a volume of 6 ml and transferred to acid washed, screw capped glass tubes.

For woodcocks, the radius and ulna were combined, and samples prepared as described above with a digestion volume of 3.0 ml and final total volume of 5ml.

Lead shotgun pellets (0.09 - 0.21g) of various sizes produced by common manufacturers in North America and Europe were digested in 4ml of trace metals grade nitric acid (HNO_3:FISHER Sci. 70%: Nepean, Ontario) and heated for 6.5 hours at 100° C. The digests were then diluted 4000 times with nanopure water for ICP-MS analysis. Blanks and duplicates (pellets from same cartridge) were concurrently prepared for quality assurance.

3.2.3 Analytical Analyses

To identify individuals with elevated Pb exposure, bone Pb concentrations were determined using a standard air-acetylene Perkin-Elmer, AAnalyst-800 flame atomic absorption spectrometer at NWRC in Hull, Quebec. Detection limit for Pb was 0.1 μg/ml and the 'functional' detection limit was determined to be 5 times this (i.e. 0.5 μg/ml). Calibration was linear from 0.0 - 5.0 μg/ml using a Pb reference solution (FISHER Sci. (CSL21-100), 1000μg/g (1 ml=1 mg Pb). Digests were measured at 217.0 nm with a slit width of 0.7 nm.

Quality assurance was maintained by concurrently digesting and analyzing reagent blanks (HNO_3 and Nanopure water), certified standard reference materials (NIST bone meal 1486: certified Pb 1.335 ± 0.014: National Institute of Standards and Technology, Gaithersburg, MD) spiked with known amounts of Pb (0.50 μg/ml. ACP Chemical Inc. Montreal, QC) and sample duplicates of the same individual with a frequency of approximately 5% per sample batch. Average percent recovery of spiked reference materials was 96.8 ± 2.42.

All samples below the flame AAS detection limit of 0.5 μg/ml were further analyzed using a Perkin Elmer AAnalyst 800 graphite furnace atomic absorption spectrometer at NWRC in Hull, Quebec. Functional detection limit was determined to be 0.01 μg/ml. Calibration was linear from 0.01 to 1.0 μg/ml.

Stable Pb isotopes were analyzed at McGill University by ICP-MS using a PE Sciex Elan 6000 and a PE Sciex Elan 5000. The instruments were operated in isotopic peak hopping mode with three measurements per peak, six repeats per integration and a total measurement time of 108 seconds. The instruments were optimized daily during use. Digests were diluted 50 times with nanopure water. Quality assurance was monitored by measuring a dilution blank (1% nitric acid and nanopure water) and a Pb isotopic standard SRM 981 (National Institute of Standards and Technology; Gaithersburg, MD) every 10 samples. Duplicates were analyzed with a frequency of approximately 5%. Instrument mass bias was corrected as described in the Elan 6000 software manual by calculating a correction factor using the equation below.

$$CF = S_{measured} / S_{known}$$

CF = Correction factor

S_{known} = the known isotope ratio of the standard

$S_{measured}$ = the measured, blank corrected isotope ratio of the standard

The correction factor was then applied to the experimental results to obtain the true ratio.

$$X_{true} = X_{measured} / CF$$

X_{true} = the true isotope ratio

$X_{measured}$ = the blank corrected isotope ratio measured by the instrument

Detector dead time is the time for which the ion counting system is unable to count incoming ions after the impact of a previous ion. This was monitored by measuring 5 different concentrations of NIST SRM 981 ranging from 0.01 – 1.0 μg/L at the beginning of each set of samples. No dead time was evident.

$Pb^{206:207}$ signatures are focused on in order to facilitate comparison to previous isotope data, however $Pb^{208:207}$ signatures are reported for future references.

3.2.4 Analysis of Previous Data

Geo-referenced data on wing-bone Pb concentrations in Mallard, American black, and Ring necked ducks from the 1989/1990 hunting season, as described in Scheuhammer and Dickson (1996), and in American woodcock from 1996, were obtained from CWS. From this national dataset, data for waterfowl wings which fell within the three study blocks of the current study were extracted, and were compared to data from 2000. Similarly, data for Pb in wing bones of American woodcock from 1996 from across eastern Canada were compared to data from 2000.

3.2.5 Data Mapping

Maps were created in ArcView 3.2 (ESRI, Redlands, CA). Spatial coordinates for source data were in degrees, minutes, seconds (dms) format and converted to decimal degrees (dd) using the software's calculator. The tabular data were converted from xy coordinates (event themes) to ArcView's native file format (shape file) in order for ArcView to read the data. The data were displayed in the Mercator projection.

3.2.6 Statistical Analysis

All bone Pb data are expressed on a dry weight basis. Raw bone Pb concentration data for waterfowl and woodcocks were not normally distributed even after various attempts at transforming the data. Therefore, a non-parametric test (Mann-Whitney U) was performed for all analyses. All statistical analyses were performed using SPSS (Version 10.0, IL, USA). All means are reported with standard deviation.

3.3 Results

3.3.1 Bone Lead Concentrations

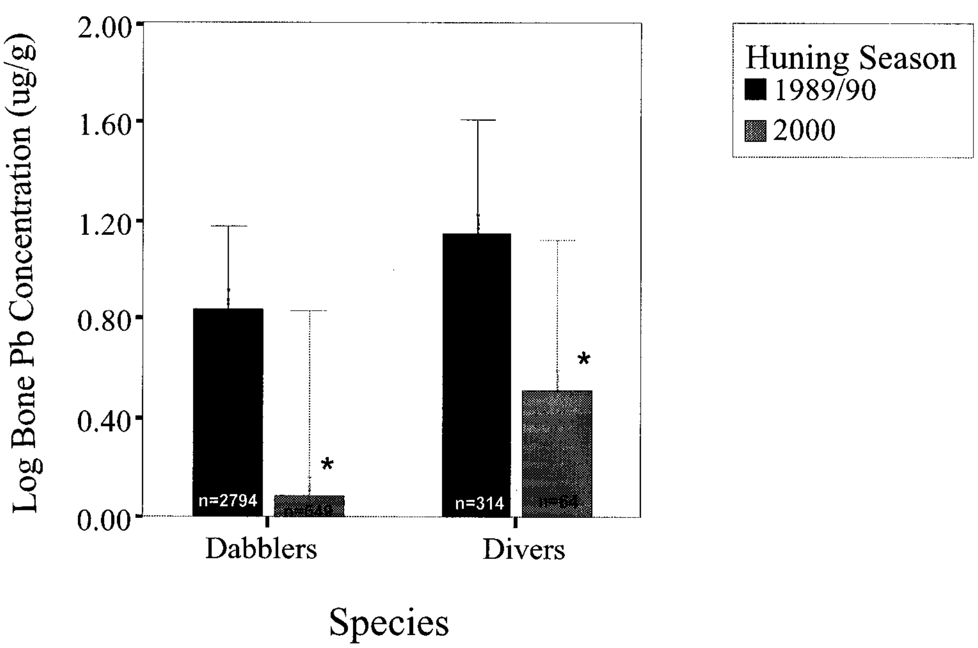
3.3.1.A Ducks

A total of 840 YY Mallard, American black duck and Ring-necked duck wings were collected of which approximately 14% were damaged and discarded, leaving 718 wings (577 Mallards, 75 American black ducks, and 65 Ring-necked ducks) for analysis. The sample size for the present study was approximately 3-6 times smaller than for the 1989/90 hunting seasons, probably because only a single hunting season's wings were used for the current study, whereas samples from two consecutive seasons were collected for the previous study (Scheuhammer and Dickson 1996), and perhaps in part because of variability in hunter success and participation in the National Harvest Survey.

For the series of duplicate samples analyzed from the same individuals, mean intra-sample variation was 8.77% (n = 42). One sample had a relative standard deviation (RSD) > 30% and was excluded from analysis. One wing had a bone Pb concentration > 400 μg/g and was removed from further analysis, consistent with Scheuhammer and Dickson (1996). Three samples had no qualifying data (eg- location shot) associated with them and another sample was lost during sample preparation. These samples were also eliminated from analyses.

There was no significant difference in average bone Pb levels between males and females, therefore data for males and females were combined for statistical analyses. Total mean bone Pb concentrations for ducks in the 2000 hunting season are compared to 1989/1990 values in Figure 3.2. Bone Pb concentrations in dabblers (Mallards and black duck combined) declined significantly from 11.32 ± 23.94 μg/g to 4.78 ±13.80 μg/g. Mean bone Pb concentrations in divers (Ring-necks) also showed a significant decrease from 28.04 ± 44.35 μg/g to 10.13 ± 18.04 μg/g.

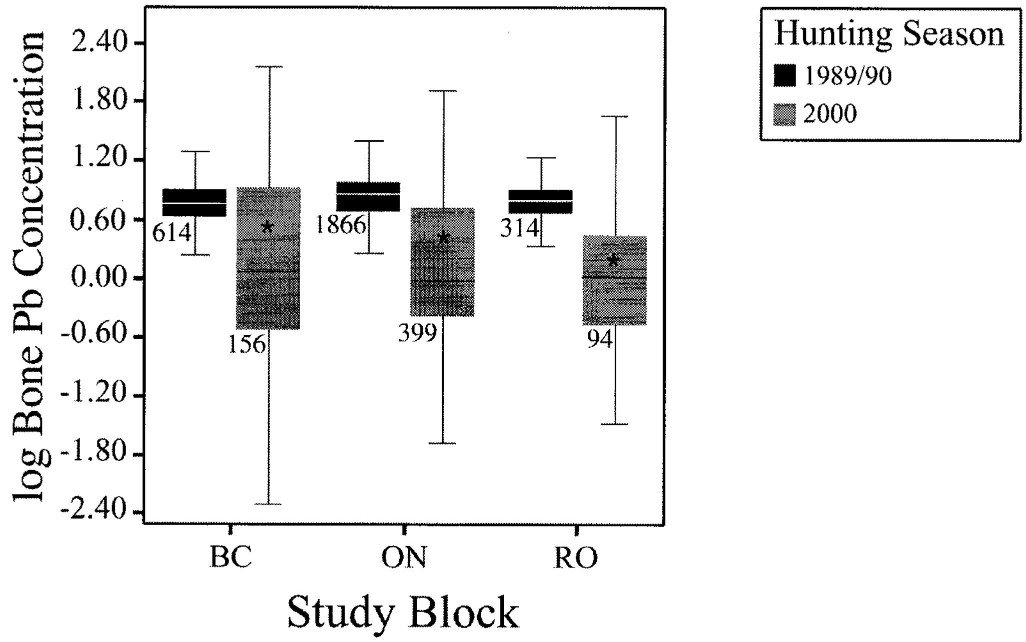
Figure 3.2: Log transformation of total mean bone Pb concentrations (μg/g) for ducks, all study blocks combined, comparing data from the 1989/1990 and 2000 hunting seasons.



* indicates significant at p<0.01

An overall decline in mean bone Pb concentrations between 1989/90 and 2000 was also observed for dabblers in each individual study region (Figure 3.3). BC dabblers showed a significant decrease in bone Pb concentrations from 11.96 ± 27.308 μg/g to 5.80 ± 13.10 μg/g. Southern Ontario and Rouyn-Noranda dabblers had bone Pb levels of 4.53 ± 13.96 μg/g and 4.17 ± 14.32 μg/g, a significant decrease from 1989/90 Pb levels of 11.46 ± 23.58 μg/g and 9.26 ± 18.35 μg/g, respectively.

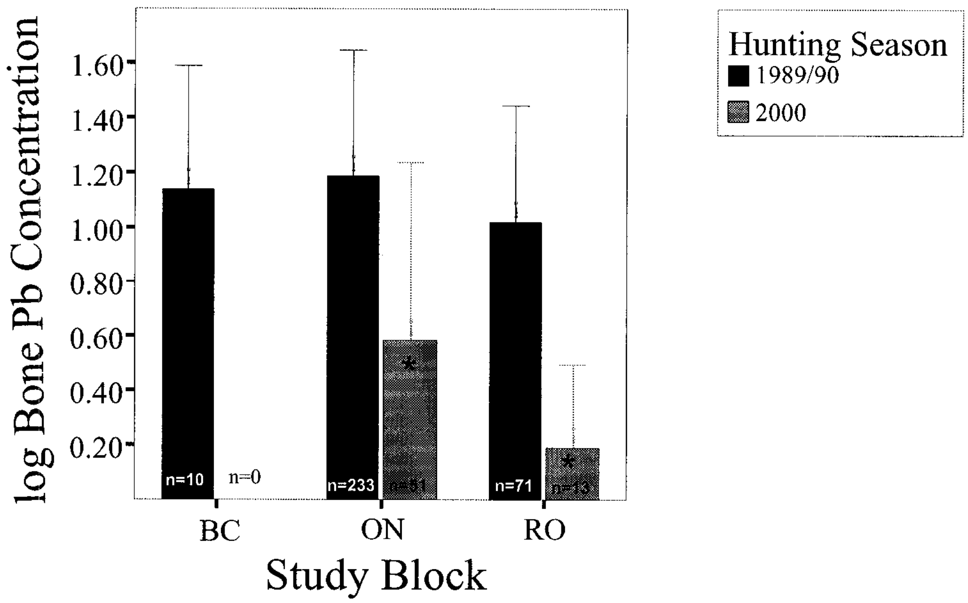
Figure 3.3 Mean bone Pb concentrations (μg/g) in dabbling ducks separated by study block for the 1989/1990 and 2000 hunting seasons



* indicates significant at p>0.01

Similarly, Ring-necked ducks (divers) showed a significant decrease between 1989/1990 and 2000 in mean bone Pb levels, from 30.48 ± 46.55 μg/g to 12.18 ± 19.70 μg/g for the 2000 hunting season in the Southern Ontario (ON) block and 20.10 ± 37.56 μg/g to 2.09 ± 2.23 μg/g in the Rouyn-Noranda (RO) block (Figure 3.4). The British Columbia study block contributed no wings from divers in the 2000 hunting season, thus a statistical comparison with the older data could not be made.

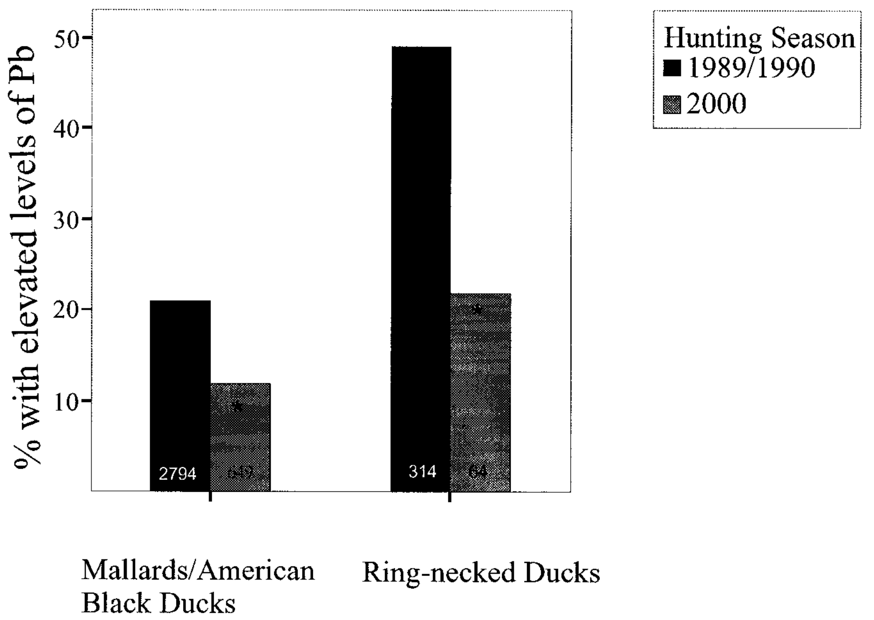
Figure 3.4 Comparison of mean bone Pb concentrations in Ring-necked ducks separated by study block for the 1989/1990 and 2000 hunting seasons



* indicates significant at p<0.01

Based on a consideration of the normal distribution curve of bone Pb concentrations for over 8600 individual YY mallard and black ducks, Scheuhammer and Dickson (1996) defined levels > 10 µg/g dry weight as 'elevated.' According to this criterion, an overall 12% of the 2000 season YY dabblers had elevated levels of bone Pb, a significant decrease from 1989/90 (21%). Additionally, the proportion of YY divers with elevated levels of bone Pb in the 2000 season (21.5%) was significantly lower than in 1989/1990 (49%) (Figure 3.5).

Figure 3.5: Proportion of dabblers and divers with elevated levels of Pb (>10 μg/g) for the 1989/1990 and 2000 hunting seasons.

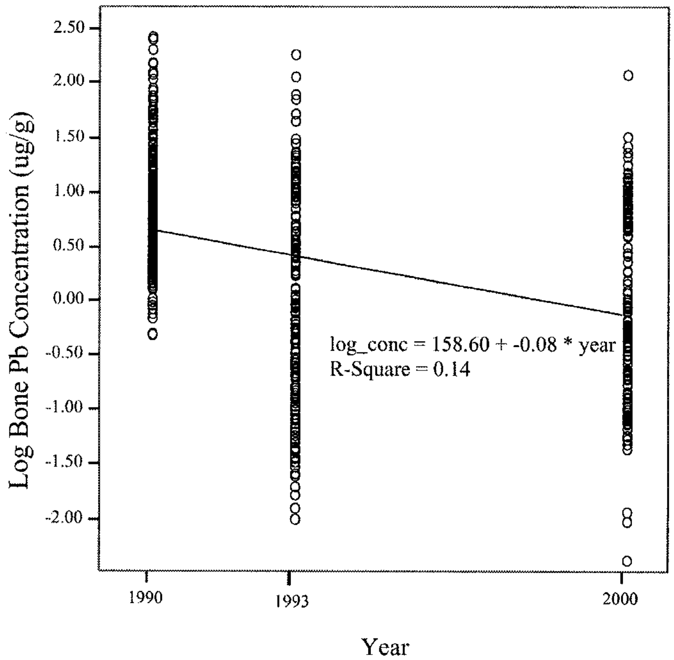


* indicates significant at p<0.01

Regionally, the proportion of dabblers in BC with elevated levels of bone Pb (16%) did not significantly decrease from the 1989/90 hunting seasons (19%). However, mean elevated bone Pb concentrations for BC dabblers with elevated bone-Pb declined from 40.62 ± 53.55 μg/g to 22.87 ± 26.30 μg/g ($p < 0.01$). Eleven percent of the southern Ontario dabblers had elevated levels of Pb, a significant decrease from the 22.5% ($p < 0.05$) in 1989/90. Mean elevated bone Pb concentrations for southern Ontario dabblers with elevated bone-Pb declined from 31.7 ± 44.04 μg/g to 24.309 ± 35.95 μg/g ($p < 0.01$). In contrast, dabblers with elevated bone Pb concentrations from the Rouyn-Noranda block showed a slight yet insignificant increase in bone Pb concentration from 1989/90 concentrations. However there was a significant ($p<0.05$) decline in the proportion (8.5%) of birds with elevated levels of Pb from the 16.2% in 1989/90.

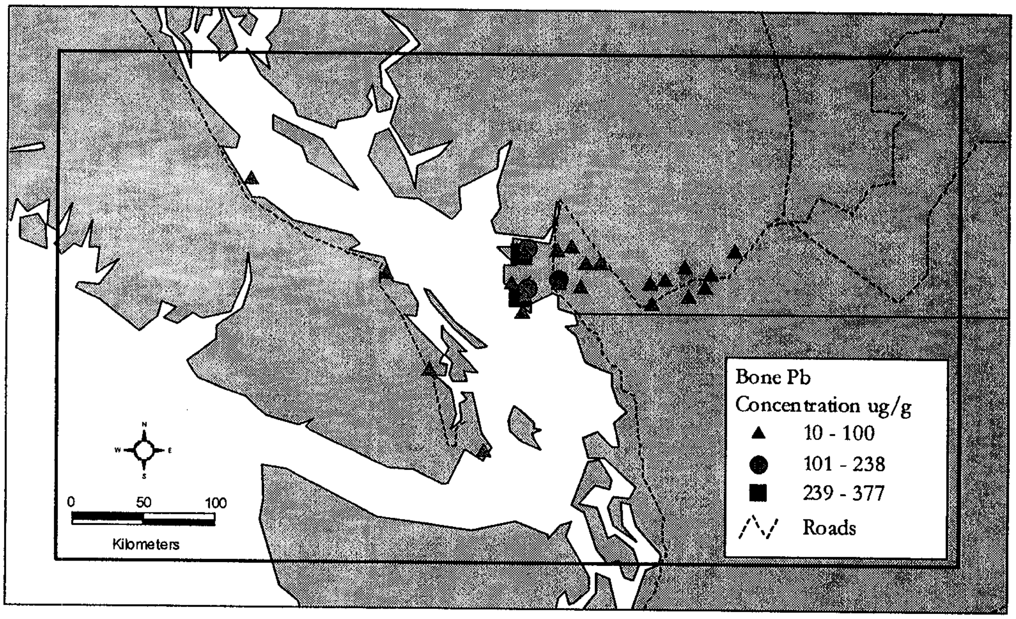
Figure 3.6 shows the regression of bone Pb concentrations in BC dabblers in 1990 before any regulations; in 1993 after the implementation of the BC non-toxic shot zone; and in 2000 after the national ban on Pb shot for waterfowl hunting. The mean bone Pb concentration in 1990 was 11.96 ± 27.31 μg/g. After the implementation of the BC non-toxic shot zone the mean bone Pb concentration decreased significantly ($p < 0.05$) to 6.36 ± 20.66 μg/g. After the 1999 national ban on Pb shot use in all areas was implemented, the mean bone Pb concentration in 2000 for this study block was further reduced to 5.80 ± 13.10 μg/g.

Figure 3.6 Regression of bone Pb concentrations in Mallards/American black ducks over the years in Canada's non-toxic shot zone in British Columbia

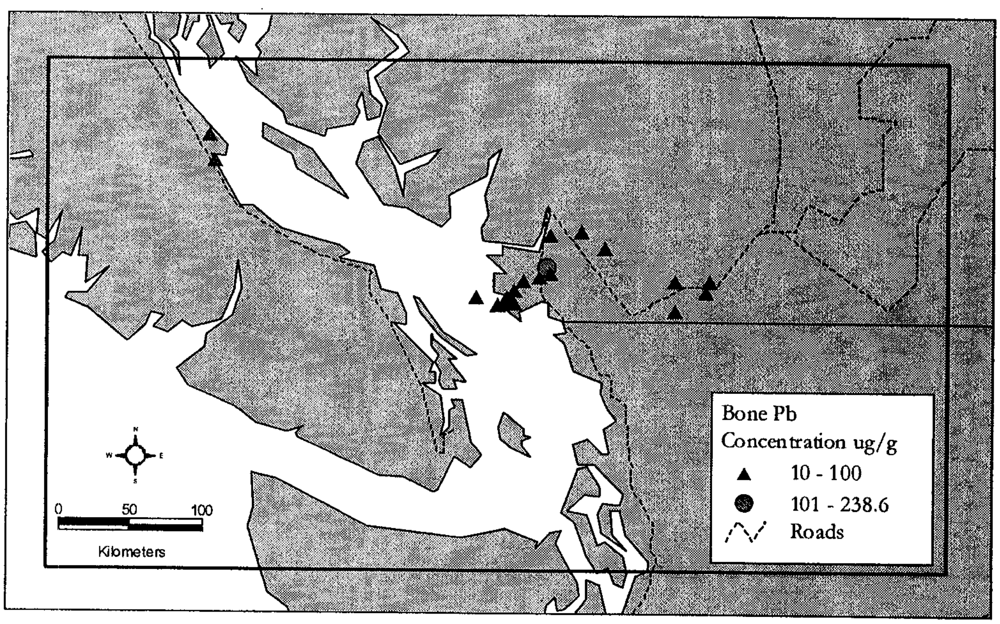


Spatial comparison of the distribution of dabblers with elevated levels of Pb (>10 μg/g) for the 1989/1990 and 2000 hunting seasons are depicted in the following maps. Figure 3.7 compares the distribution of dabblers with elevated levels of Pb for BC in 1989/1990 and 2000. Figure 3.8 compares the distribution of Ontario dabblers with elevated levels of Pb for the 1989/1990 and 2000 hunting seasons. Figure 3.9 compares the distribution of dabblers with elevated levels of Pb in Rouyn-Noranda for 1989/1990 and 2000.

Figure 3.7: Geographical distribution of dabblers with elevated bone-Pb levels in BC for the 1989/1990 and 2000 hunting season

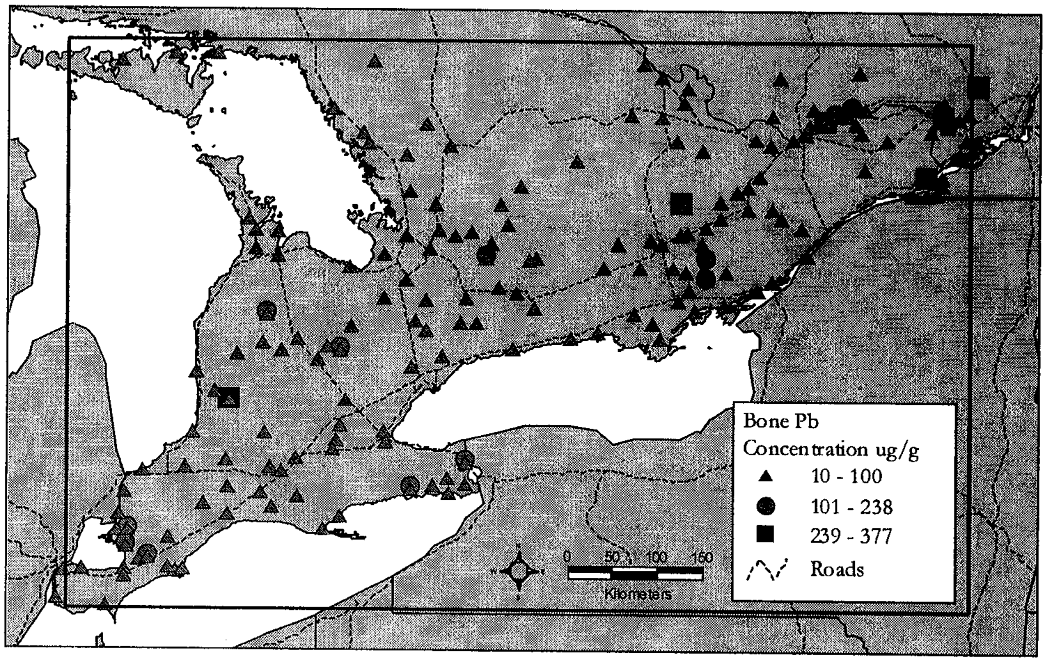


1989 – 1990

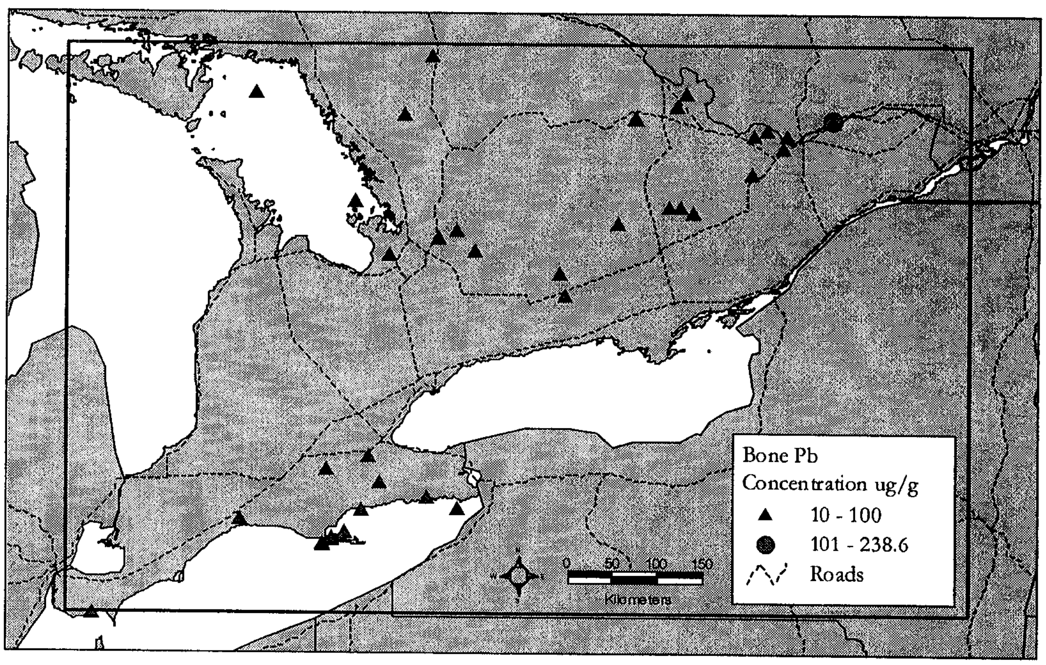


2000

Figure 3.8: Geographical distribution of dabblers with elevated bone Pb levels in Southern Ontario for the 1989/1990 and 2000 hunting season

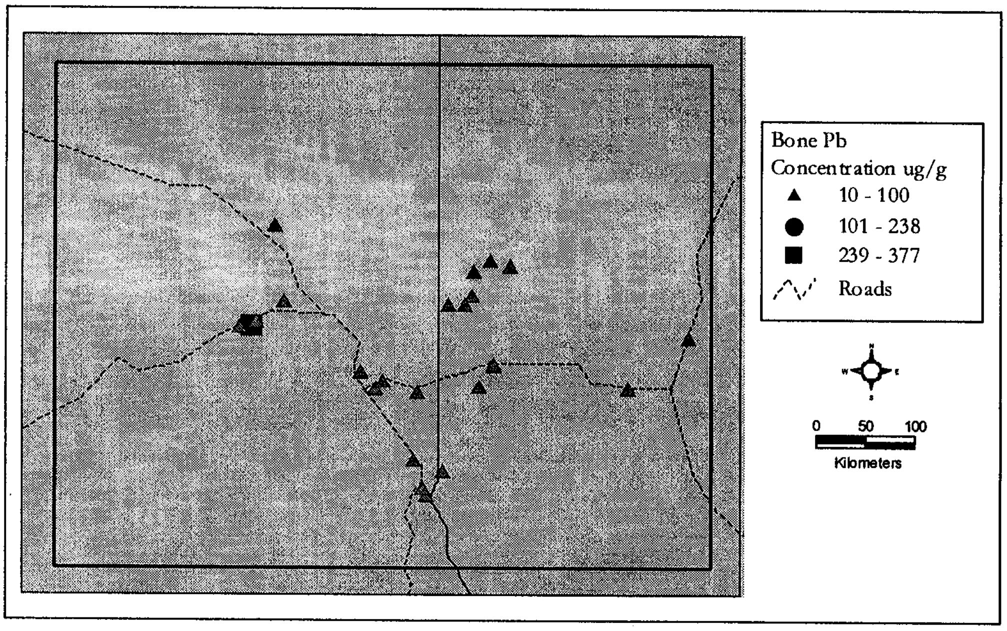


1989 – 1990

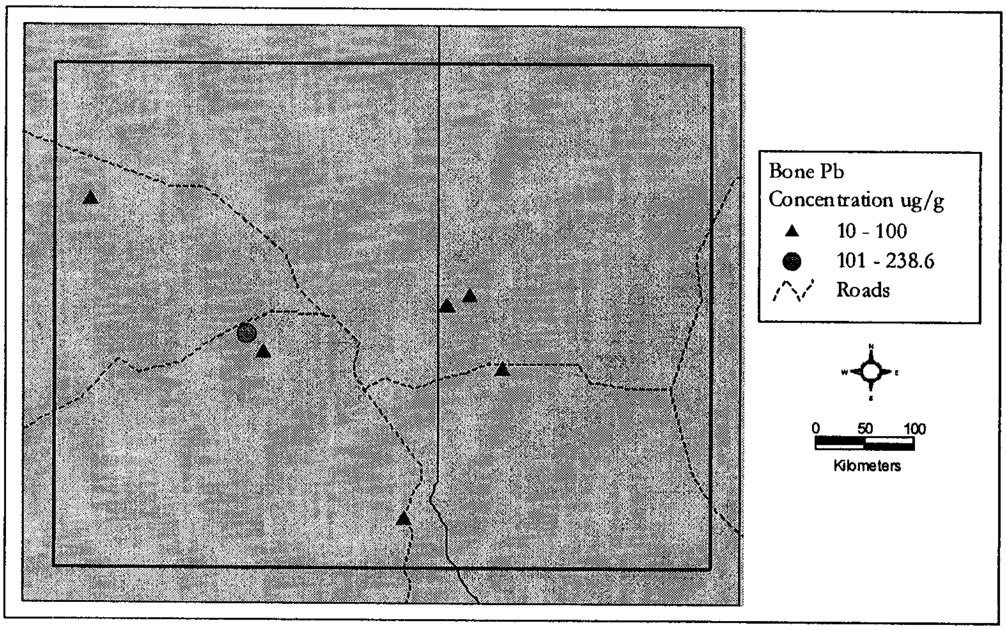


2000

Figure 3.9: Geographic distribution of dabblers with elevated bone Pb levels in Rouyn-Noranda for the 1989/1990 and 2000 hunting season



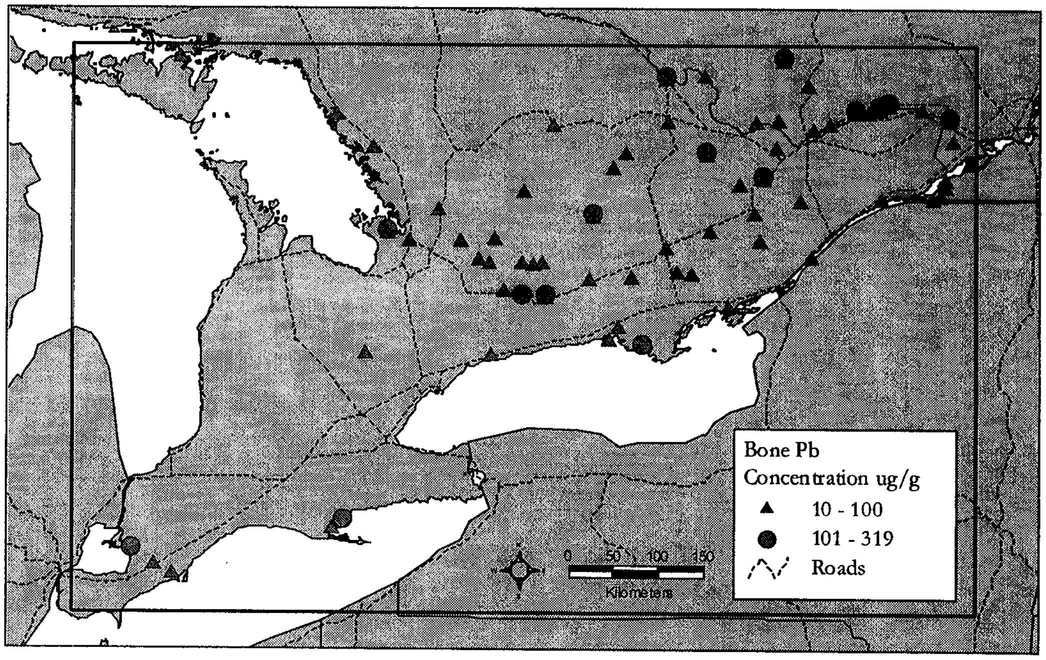
1989 - 1990



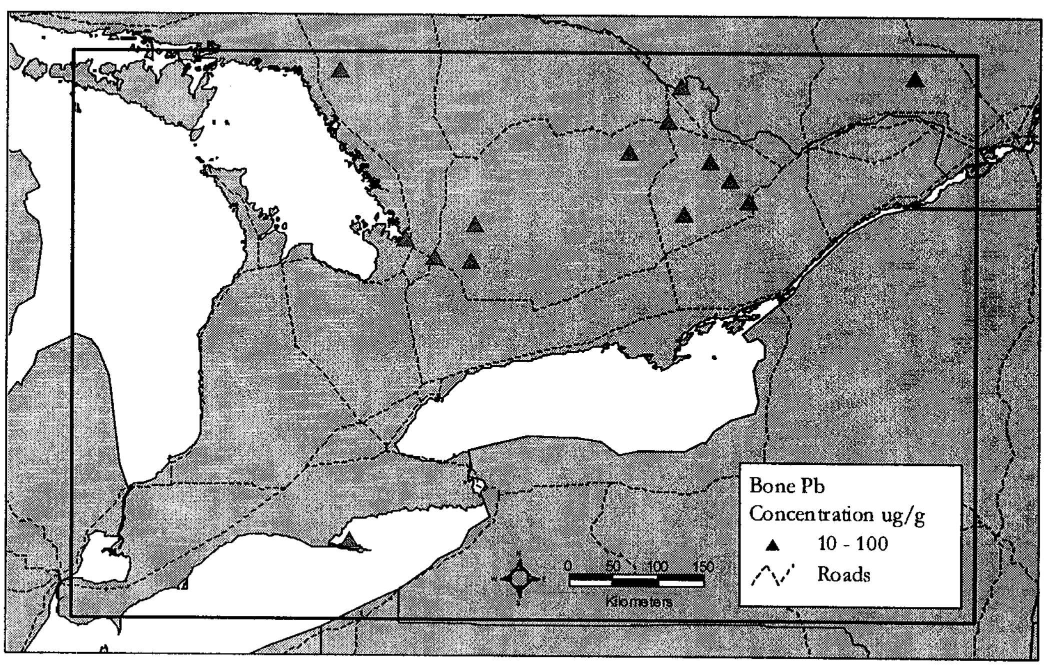
2000

Spatial distribution of elevated bone Pb concentrations of Ring-necked ducks from the southern Ontario block is depicted in Figure 3.10 for both the 1989/1990 and 2000 hunting seasons. No maps were constructed for either British Columbia or Rouyn-Noranda, as wings of this species for these study blocks had no bone Pb concentrations greater than 10 μg/g.

Figure 3.10: Geographical distribution of Ring-necked ducks with elevated bone Pb levels in Southern Ontario for the 1989/1990 and 2000 hunting season



1989 – 1990



2000

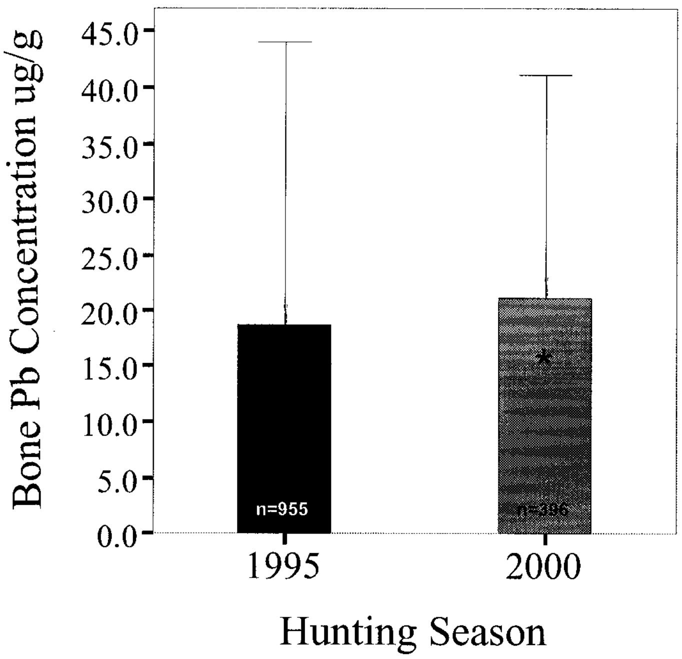
3.3.1B American woodcocks

Approximately 650 American woodcock wings were submitted, of which approximately 12% were discarded due to damaged bones. Bone Pb concentrations were analyzed for 579 undamaged wings, of which 115 were adults from Ontario and Quebec and 398 were YY from Ontario, Quebec, New Brunswick and Nova Scotia. Fifty-eight wing samples had no associated data, therefore age, sex and location of collection for these samples are not known and they are not included in the statistical analysis. Additionally, 10 wings were classified as "unknown" for age and were not included in statistical analyses. In order to ensure that Pb exposure was from within Canada, data from adult woodcocks were not included in the statistical analysis.

For the series of duplicate samples analyzed from the same individuals, mean intra-sample variation was 7.64% relative standard deviation (n=25). One sample had a % RSD > 30% and was excluded from analysis.

Figure 3.11 depicts the total mean bone Pb concentrations for YY American woodcocks across Eastern Canada for the 1995 and 2000 hunting seasons. Unlike waterfowl, YY woodcocks showed a small but significant increase ($p < 0.05$) in mean bone Pb concentrations between 1995 and 2000 from 18.69 ± 25.45 µg/g to 21.21 ± 19.96 µg/g, respectively.

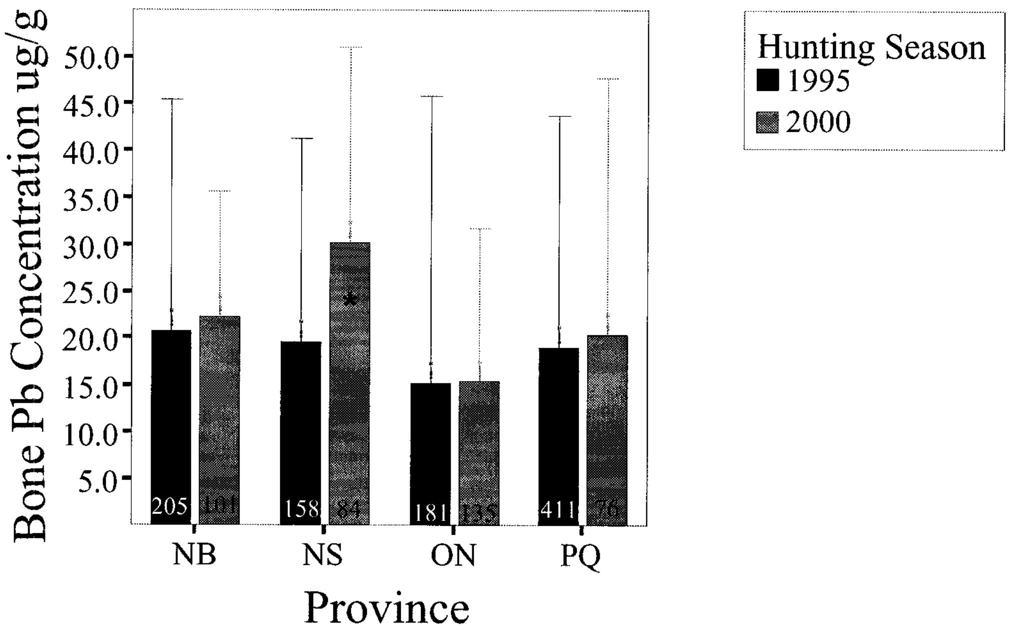
Figure 3.11 Total mean bone Pb concentrations for YY American woodcocks from across Eastern Canada for the 1995 and 2000 hunting seasons



* indicates significant at p<0.01

On a regional basis, only Nova Scotia YY woodcocks showed a significant increase in mean bone Pb concentrations between the 1995 and 2000 hunting seasons from 19.51 ± 21.60 μg/g to 30.27 ± 20.66 μg/g (Figure 3.12). There was no significant increase in mean bone Pb concentration between the 1995 and 2000 hunting seasons in Ontario, Quebec or New Brunswick YY woodcocks.

Figure 3.12: Mean Pb concentrations (μg/g) YY American woodcocks separated by Province for the 1995 and 2000 hunting seasons.



* indicates significant at $p<0.01$

Scheuhammer et al. (1998) established a value of 20 μg/g as elevated bone Pb concentration in woodcocks. According to this criterion, 40.5% (n=509) of the woodcock wings collected in 2000 showed elevated levels of Pb, of which approximately 27% were adults and 73% were YY. Sixty-six percent of Nova Scotia's YY woodcocks collected in 2000 had elevated levels of Pb, a significantly higher proportion then YY woodcocks in 1995 (32%). The remaining provinces: Ontario (21%), Quebec (32%) and New Brunswick (43%) did not have significantly higher proportions of elevated levels of Pb in YY woodcocks then 1995.

Young of the year woodcocks with elevated levels of bone Pb in New Brunswick had significantly ($p<0.05$) higher Pb concentrations in 2000 then YY woodcocks in 1995. There was no significant difference in bone Pb levels of YY woodcocks with elevated levels of Pb in Ontario, Quebec or Nova Scotia.

Quality Assurance of ICP-MS

The Elan 6000 and Elan 5000 instruments showed a significant difference in precision and accuracy, with the Elan 6000 showing a %RSD of 0.18 for the $Pb^{206:207}$ ratio and the Elan 5000 showing a 1.67 % RSD.

The measured mean $Pb^{206:207}$ and $Pb^{208:207}$ ratios for the Pb isotopic standard analyzed by the Elan 6000 was 1.093 ± 0.002 and 2.364 ± 0.003, respectively. Certified values of $Pb^{206:207}$ and $Pb^{208:207}$ ratios for the Pb isotopic standard SRM 981 are reported as 1.093 and 2.370. The Elan 5000 measured the mean $Pb^{206:207}$ and $Pb^{208:207}$ ratios for the Pb isotopic standard as 1.095 ± 0.02 and 2.361 ± 0.008, respectively. Duplicate digests for ducks had a mean % RSD for the $Pb^{206:207}$ of 0.17 and woodcocks had a mean % RSD of 0.32.

Pb shot pellets

Pellets from 13 common brands of shotshell ammunition manufactured in Europe and North America were analyzed (Table 3.1). The mean with-in cartridge % RSD for the $Pb^{206:207}$ was 0.17. Although there was considerable variation in $Pb^{206:207}$ between different brands of shot, all samples had ratios higher than Pb ores from Canadian Precambrian mining sources (Brown 1962), with an overall mean of 1.157 ± 0.05. Mean $Pb^{208:207}$ was 2.44 ± 0.04. Approximately, 38% of the shot pellets had ratios in the range that characterizes Pb from combustion of leaded gasoline in eastern Canada (Sturges and Barrie, 1989).

Scheuhammer and Templeton (1996) reported a mean $Pb^{206:207}$ of 1.20 (n=45) for North American shotgun pellets of various sizes and manufacturers. Combining these data with additional North American pellets from the current analysis, a mean $Pb^{206:207}$ of 1.19 ± 0.04 (n=58) was observed.

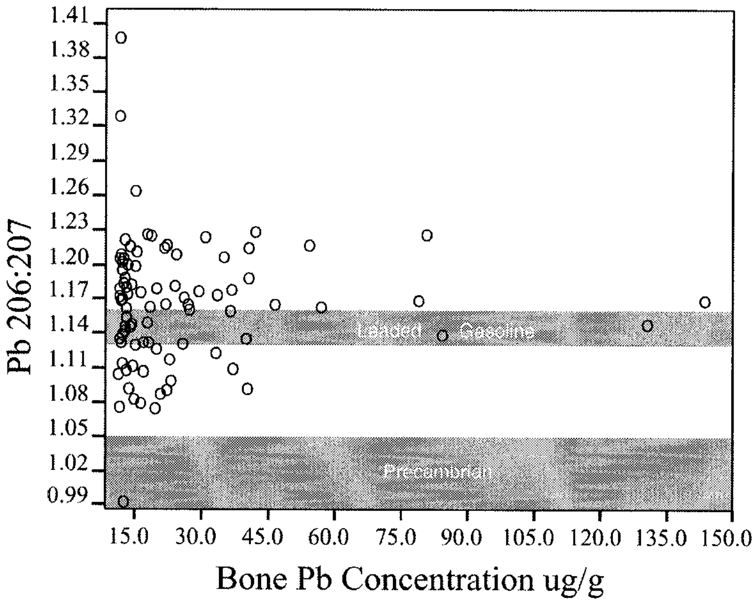
Table 3.1 Lead shotgun Pellets from North America and Europe analyzed on ICP-MS

Manufacturer	Location	Year	Shot size	No. of Pellets	Weight (g)	**$Pb^{206:207}$**
Humasson	Ontario	2000	8	2	0.1430	**1.22**
Challenger	Quebec	2000	8	2	0.1346	**1.16**
CIL "Canuck"	Quebec	1976	12	8	0.1015	**1.08**
Remington	USA	1992	9	3	0.1514	**1.23**
Winchester	USA	1980	4	1	0.2124	**1.15**
Kent	USA	2000	8-coated	2	0.1382	**1.10**
Federal	USA	2000	8	2	0.1256	**1.23**
Eley Co.	UK	1996	5	1	0.1567	**1.08**
Vee	Spain	2001	7.5	2	0.1735	**1.15**
Sellier & Bellot	Czech Republic	2000	unknown	2	0.1554	**1.17**
Douillerie	France	1991	7.5	1	0.0943	**1.16**
PD Olympic	Poland	1991	4	1	0.2073	**1.16**
Mondial	Hungary	1991	7.5	2	0.1702	**1.17**
Mean ± SD						**1.16 ± 0.05**

Ducks

Seventy-four YY dabblers with elevated (≥ 10 μg/g) levels of Pb and 77 YY dabblers with 'non-elevated' Pb levels (<10 μg/g) were analyzed for stable Pb isotopes using ICP-MS. Due to the low sensitivity of the ICP-MS and the calcium-rich samples, wing-bones containing less then 2 μg/g of Pb were not analyzed. Thirteen divers with 'elevated' and 2 with 'non-elevated' levels of Pb were also analyzed using ICP-MS. Figure 3.13 depicts the $Pb^{206:207}$ ratios in relation to bone Pb concentrations in both dabblers and divers for the 2000 hunting season (isotope ratios were not available for the 1989/90 season samples). Mean $Pb^{206:207}$ for Mallards/American black ducks and Ring-necked ducks in all three study blocks combined was 1.17 ± 0.05 and 1.17 ± 0.04, respectively. Overall mean $Pb^{208:207}$ ratios were 2.42 ± 0.07 for Mallards/American black ducks and 2.43 ± 0.03 for Ring-necked ducks.

Figure 3.13: $Pb^{206:207}$ signatures for wings with elevated bone Pb concentrations (>10 μg/g) in dabblers and divers of all three study blocks



An overall comparison of mean $Pb^{206:207}$ signatures in wingbones of dabblers with elevated (> 10 μg/g) vs. 'non-elevated'(<10 μg/g) levels of bone Pb showed no significant difference.

In regional comparisons, mean $Pb^{206:207}$ and $Pb^{208:207}$ signatures in wingbones of dabblers with elevated (> 10 μg/g) vs. 'non-elevated'(<10 μg/g) levels of bone Pb in BC, ON and RO is depicted in Table 3.2. A significant difference in $Pb^{206:207}$ isotope ratios between 'elevated' and 'non-elevated' individuals was observed for BC, but not for ON or RO birds. There was no significant difference in 'non-elevated' mean $Pb^{206:207}$ signatures between the three study blocks, however for 'elevated,' mean $Pb^{206:207}$ signatures there were significant ($p<0.05$) differences between BC and ON and between ON and RO. There was no significant difference in mean $Pb^{206:207}$ signatures for birds with elevated Pb levels between BC and RO. Within the 'non-elevated' RO dabblers, a single outlier had a $Pb^{206:207}$ of 1.03 which reduced the mean isotope signature. The removal of this outlier, brought the mean $Pb^{206:207}$ to 1.15.

Table 3.2 Mean $Pb^{206:207}$ and $Pb^{208:207}$ for BC, ON and RO dabblers with elevated levels of Pb in comparison to dabblers with non-elevated levels of Pb (N).

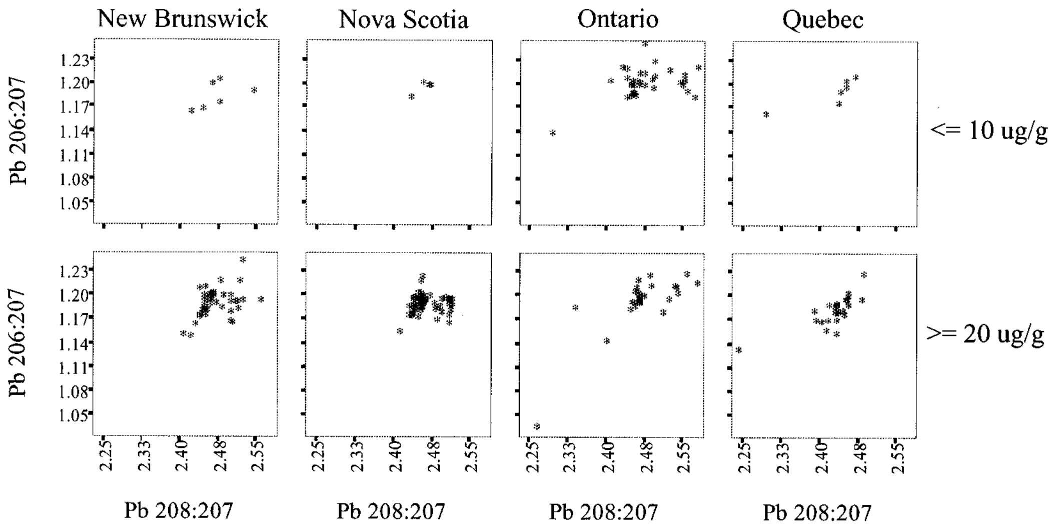
Study Block	Mean $Pb^{206:207}$		Mean $Pb^{208:207}$	
	<10 μg/g	>10 μg/g	<10 μg/g	>10 μg/g
British Columbia (BC)	1.19 ± 0.07 (31)	1.15 ± 0.05 (25)	2.35 ± 0.28	2.41 ± 0.04
Southern Ontario (ON)	1.19 ± 0.04 (39)	1.19 ± 0.04 (41)	2.34 ± 0.29	2.43 ± 0.09
Rouyn-Noranda (RO)	1.13 ± 0.08 (5)	1.15 ± 0.04 (7)	2.40 ± 0.06	2.40 ± 0.03

Southern Ontario is the only study block which had Ring-necked ducks showing elevated levels of Pb, therefore the mean $Pb^{206:207}$ remains 1.17 ± 0.04 as mentioned above. There is no significant difference in mean $Pb^{206:207}$ signatures between 'non-elevated' and 'elevated' wingbones of Ring-necked ducks.

American Woodcocks

Figure 3.14 compares the $Pb^{206:207}$ and $Pb^{208:207}$ signatures of YY woodcocks from eastern Canada with elevated and non-elevated levels of Pb. Mean $Pb^{206:207}$ for YY woodcocks with elevated (1.18 ± 0.02) and 'non-elevated' (1.19 ± 0.02) levels of Pb were significantly different ($p = 0.013$). One wing-bone with an elevated bone Pb level fell into to the Canadian Precambrian Pb ore range (<1.07) while 8% and 11% of YY woodcocks with 'non-elevated' and elevated levels of Pb, respectively, fell into the narrow range for leaded gasoline additives used in eastern Canada (1.13-1.16).

Figure 3.14 Comparison of YY American woodcocks Pb $^{206:207}$ and $Pb^{208:207}$ for bone Pb concentrations of 10 μg/g and 20 μg/g.



Mean $Pb^{206:207}$ and $Pb^{208:207}$ signatures for YY woodcocks are shown in Table 3.3 for each province. Mean $Pb^{206:207}$ signatures for 'non-elevated' YY woodcocks were significantly ($p<0.05$) different between Ontario and New Brunswick but not between the remaining provinces. Mean $Pb^{206:207}$ signatures for 'elevated' YY woodcocks were significantly different between Ontario and Quebec ($P<0.01$); Ontario and Nova Scotia ($p<0.05$); and Quebec and Nova Scotia ($p<0.05$), but were not significant for the remaining provinces.

Table 3.3 Comparison of mean $Pb^{206:207}$ and $Pb^{208:207}$ signatures for YY woodcocks with bone Pb concentrations of ≥ 20 μg/g and ≤ 10 μg/g in Ontario, Quebec, New Brunswick and Nova Scotia.

	Young of the Year					
	≥ 20 μg/g			≤ 10 μg/g		
Province	N	$Pb^{206:207}$	$Pb^{208:207}$	N	$Pb^{206:207}$	$Pb^{208:207}$
Ontario	27	1.19 ± 0.04	2.47 ± 0.06	33	1.20 ± 0.02	2.48 ± 0.07
Quebec	24	1.18 ± 0.02	2.43 ± 0.05	6	1.18 ± 0.02	2.42 ± 0.06
New Brunswick	42	1.18 ± 0.02	2.47 ± 0.03	6	1.18 ± 0.02	2.47 ± 0.04
Nova Scotia	55	1.18 ± 0.01	2.47 ± 0.03	4	1.19 ± 0.01	2.46 ± 0.02

3.3 Discussion

3.3.1 Ducks

A major focus of this research was to shed light on the relative importance of the three main sources of Pb exposure in three species of waterfowl (Mallards, American black ducks and Ring-necked ducks) and one upland game bird (American woodcock) with the use of stable Pb isotopes. In addition, verification of hunter compliance with the ban on Pb shot and effectiveness of the ban will be addressed (see Chapter 4 for additional discussion).

It has been determined that the ingestion of Pb shot pellets was the primary source of Pb exposure in many game birds (Sanderson and Bellrose 1986; Kendell et al. 1996; Scheuhammer and Templeton 1995; Scheuhammer and Dickson 1996). However, additional sources of concern include: Pb particles deposited in to the environment from past burning of leaded gasoline, mining, smelting, and municipal waste incineration.

Attempts at reducing the amount of Pb deposited into the environment and subsequently available to humans and wildlife have led to a number of regulations concerning the use of Pb. In Canada, a ban on the use of Pb shot for hunting migratory birds (except American woodcocks, Mourning doves and Band tailed pigeons) within 200 meters of any body of water was put into effect on September 1, 1997. This ban was extended to include all areas of land and water on September 1, 1999. Further reductions in the amount of Pb pellets deposited into the environment may be attributed to the decline in the number of hunters. Nationwide, migratory game bird hunting permit sales have declined since 1978 with an average annual decrease of 17,558 permits (Levesque and Collins 1999). Additional restrictions on Pb emissions, such as the removal of Pb additives in gasoline and stricter restrictions on industrial releases into the environment have helped reduce the amount of Pb deposited into the Canadian environment.

Life-long exposure to Pb is best estimated by measuring Pb in bones, as bone tissue has a high affinity for Pb and Pb is typically immobilized upon deposition. However, the definition of 'elevated' concentrations of Pb in avian bones has been difficult to quantify in a 'one size fits all' variable, as Pb absorption is dependent upon species, sex, diet and environmental factors. Finley and Dieter (1978) investigated the influence of laying on Pb accumulation in bone of mallard ducks. They reported birds dosed with one or two No. 4 Pb shot to have bone Pb levels ranging from 5.0 - 488 μg/g while control birds contained < 5 μg/g (dry weight) of bone-Pb. Finley et al.. (1976) reported that juvenile male Mallards dosed with one No. 4 Pb shot had an average of 10 μg/g (dw) of Pb in wing bones, 5 weeks after dosing, while control juvenile birds averaged 4 μg/g. Nineteen Canada geese known not to be suffering from Pb poisoning had bone Pb concentrations that ranged from 2 – 11 μg/g, while an additional 80 birds that had died of Pb poisoning contained 7-389 μg/g of Pb in their bones (Szymczak and Adrian 1978). Bagley and Locke (1967) evaluated individuals of 13 species of wild birds with no apparent signs of Pb toxicity for Pb concentrations in the tibia in order to obtain a baseline level of 'background' Pb. Mean concentrations ranged from 2 μg/g (wet weight) in Canada geese (n=11) to13 μg/g (wet wt.) in Snow geese (*Chen hyperborea*) (n=18). Mallards had a mean bone Pb concentration of 10 μg/g (n=6) with a range of 6-14 μg/g. Pain (1991) judged bones of waterfowl containing less then 10 μg/g of Pb to be reflective of 'background' levels.

However, YY birds should have uniformly low levels of bone Pb (≤ 2 μg/g), acquired from natural geological sources, unless they have been exposed to a large amount of environmental Pb in their short life span (Scheuhammer and Dickson 1996). For this reason, they are useful in monitoring potential local sources of environmental Pb exposure. In the early 1970's, Stendell et al. (1979) documented median bone Pb concentrations of < 2 μg/g in juvenile Lesser scaup, Northern pintails (*Anas acuta*), Canvasbacks (*Aythya valisineria*) and Mallards. Mean bone Pb concentrations of 17 non-exposed immature eagles collected from the Canadian Prairie provinces was 2.5 μg/g (dry wt) (Wayland et al.. 1999).

In the present study, YY Mallards/American black and Ring necked ducks collected from the three study blocks showed significant decreases (58%) in mean bone Pb concentrations, when compared with mean bone Pb levels of YY waterfowl from 1989/90. Although these decreases are dramatic, a substantial proportion of YY ducks continue to show intermediate levels of bone Pb above normal background exposure (≤ 2 μg/g).

Southern Ontario and Rouyn-Noranda YY dabblers showed overall mean bone Pb concentrations less then 5 μg/g and a significant decrease in the proportion of birds with elevated levels of Pb (11% and 9% respectively). Likewise, mean bone Pb levels in Ring-necked ducks have significantly declined in mean bone Pb levels as well as in the proportion of birds with elevated levels of Pb (21.5%), have declined significantly. Due to the feeding behavior of Ring-necked ducks, bone Pb concentrations were about three times greater then the dabblers. This is in close agreement with the 1989/90 results and Anderson et al.'s (2000) findings, indicating that Ring-necks continue to have higher Pb shot ingestion rates then dabblers and thus accumulate higher concentrations in the bone tissue. The higher ingestion rate found in Ring-necked ducks (and many other diving ducks) is attributed to feeding habits(Kennedy and Nadeau 1993).

British Columbia dabblers have an overall mean bone Pb concentration of about 6 μg/g, however the proportion of birds with elevated levels of Pb (16%) has not significantly changed from 1989/90 levels (19%), and exceeds the 10% shot ingestion rate criteria set for Canadian 'nontoxic shot zones.' A series of bone Pb level measurements in YY dabblers prior to Pb shot restrictions (1989/90), two years after the implementation of a 'nontoxic shot zone' (1993), and one year after the national ban (2000) show that bone Pb levels dropped precipitously from 1989/90 to 1993, but exhibited little or no further decline from 1993 to 2000. This consistency in bone Pb levels and proportion of dabblers with elevated levels of Pb may be an indicator that either: 1) Pb shot use by hunters had already ceased by 1993, and Pb shot is no longer the primary source of Pb exposure in these birds; or 2) the level of noncompliance with the restrictions of Pb shot among hunters (i.e. the number of hunters illegally using Pb shot) in the BC study region has remained relatively constant between 1993 and 2000.

Spatial distributions of ducks with elevated bone Pb concentrations have changed notably from 1989/90. Declines in high levels of Pb are most prominent in areas previously characterized as high or moderate hunting intensities (Dickson and Scheuhammer 1993). For example: in the BC block, dabblers with elevated bone Pb concentrations show a notable decrease along the coast near Duncan on Vancouver Island and in the Fraser River Delta area; in the ON study block, dabblers with elevated bone Pb concentrations have declined along the Ottawa river near Arnprior and Ottawa city as well as significant declines in the Peterborough and Niagara Falls areas. For the RO study block, apparent declines in dabblers with elevated bone Pb concentrations are visible in the Kettle Lakes Provincial Park area and near Notre Dame de Nord.

The decrease in overall mean bone Pb concentrations in waterfowl has directly followed restrictions on the use of Pb shot ammunition first implemented in the fall of 1990 in Canada with the selection of several 'nontoxic shot zones.' The decrease in proportions of birds with elevated levels in of Pb in the ON and RO blocks in conjunction with the decrease in bone Pb concentrations and an increase in restrictions on the use of Pb ammunition is consistent with the conclusion that Pb shot was the primary source of Pb exposure to waterfowl in these areas. However, for BC, there was no significant difference in proportions of birds with elevated levels of Pb, indicating that perhaps these birds are exposed to a significant source of environmental Pb other than Pb shot pellets.

Lead from an ore body has a permanent isotopic composition which varies among different ores depending on the geological history of the deposit. There are four stable Pb isotopes (i.e. 204, 206, 207 and 208). The relative amounts of these isotopes remain unaltered by normal physical and chemical processes. Thus with a knowledge of the isotope signatures of various sources of Pb, by measuring Pb isotopes in the wing-bones of wild birds, we may obtain valuable information on the relative importance of different sources of Pb exposure.

Stable Pb isotope ratios have previously been used to differentiate sources of environmental Pb. Sturges and Barrie (1987) used Pb isotopic signatures to differentiate Canadian and US sources of Pb emissions. Lead used in gasoline in Canada comes from a few select mines with the narrow $Pb^{206:207}$ signature of 1.13-1.16. Lead isotopes were used to discriminate between sources of Pb in surface soils of rural and urban areas near Adelaide, South Australia. It was documented that Pb in the surface horizons was derived mainly from the combustion of leaded gasoline (Gulson et al. 1981). Scheuhammer and Templeton (1996) used $Pb^{206:207}$ signatures to determine sources of Pb exposure in wild birds. They reported the range of $Pb^{206:207}$ ratios in tissues of waterfowl and raptors with elevated Pb exposure to be similar to that for Pb shot pellets whereas juvenile herring gulls exhibited a mean isotope ratio (1.14) more characteristic of the Pb added to gasoline used in Canada.

Stable Pb isotopes were used in the present study in an attempt to identify the primary sources of Pb exposure in birds with elevated levels of Pb, or at least to identify and eliminate from consideration those sources that were not major sources of exposure for wild birds. For this study, $Pb^{206:207}$ signatures were used in order to compare pre and post ban data. Pb208:207 signatures have been reported for future reference but are not discussed in detail has these signatures were not reported in previous studies. Sangster et al. (2000) documented that the combination of Pb^{206}, Pb^{207} and Pb^{208} ratios correctly classified about 86% of sources. Although omission of the Pb^{204} ratios resulted in almost an 11% misclassification, Pb^{204} is often not accurately measurable due to its low concentration in many ores and the relatively low precision of the ICP-MS.

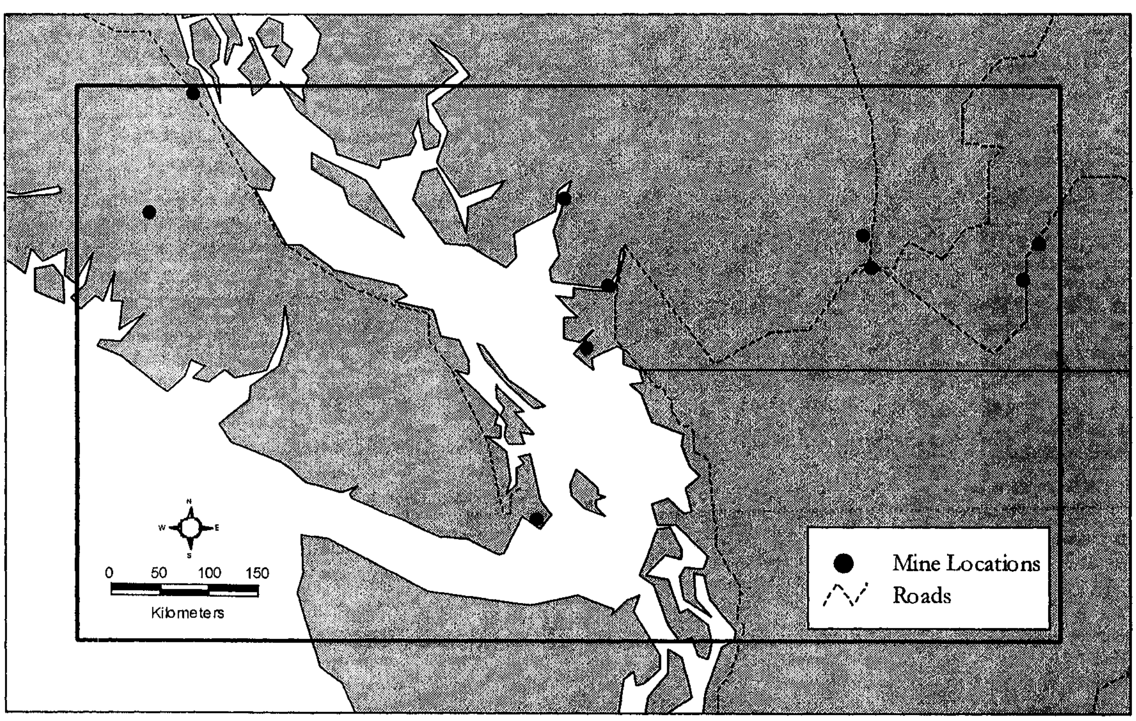
Approximately 80% of the Pb shot imported into Canada originates from three main U.S. manufacturers: Winchester, Federal and Remington (Scheuhammer and Norris 1995). Domestically, Canada produced relatively little of its own Pb shot. Birds exposed to Pb shot typically used in Canada demonstrate a wide range of $Pb^{206:207}$ signatures (1.08-1.27) with a mean of 1.19 (Scheuhammer and Templeton 1996; present study). $Pb^{206:207}$ signatures for Canadian Precambrian Pb ore do not exceed 1.07 (Brown 1962), while current Pb ore mines have a range of 1.07-1.27, with a mean of 1.18 for 35 Canadian mines (Sangster et al. 2000). The Pb ore used to manufacture anti-knock gasoline additives typically used in Canada came from a few select mines with the narrow $Pb^{206:207}$ range of 1.13-1.16, with a mean of 1.15 (Sturges and Barrie 1987).

Birds with elevated levels of Pb have typically been exposed to Pb from anthropogenic sources and therefore might well have different isotope ratio than birds with non-elevated levels of Pb.

The dramatic decline in bone Pb levels after the ban went into effect indicates that the major source of lead exposure, pre-ban, was due to lead shot pellets. A comparison of dabblers in BC showed a significant difference in $Pb^{206:207}$ signatures between birds with elevated levels of Pb (>10 μg/g) and those with non-elevated levels of Pb (< 10 μg/g), indicating that birds with elevated levels of Pb are being exposed to a different source of Pb than birds with non-elevated levels of Pb. The mean $Pb^{206:207}$ signature (1.15) for dabblers with elevated Pb in BC resembles most closely the mean signature for Canadian leaded gasoline, indicating that Pb deposited into the environment during the years of leaded gasoline use may still be bioavailable to wildlife. Pb particles for the combustion of leaded gasoline tend to be found in cities and along roadside habitats (Gish and Christensen 1973). Additionally, Pb is still used in jet fuel, marine and off-road vehicles and large machinery.

The $Pb^{206:207}$ signature (1.19) for non-elevated dabblers most closely resembles the mean signature for Pb shot, indicating that these 'non-elevated' birds may have ingested a single Pb pellet, or soil/sediment with Pb particles made bioavailable through the erosion of Pb pellets, producing above background levels of Pb, but not necessarily elevated levels. However, the BC study block has a history of mining (Figure 3.15), which may be a source of Pb exposure for these birds. The mean $Pb^{206:207}$ signature for two active mines (Duncan and Jordan River mines) within the study block is 1.19 (Sangster et al. 2000).

Figure 3.15 Mine locations in the BC study block

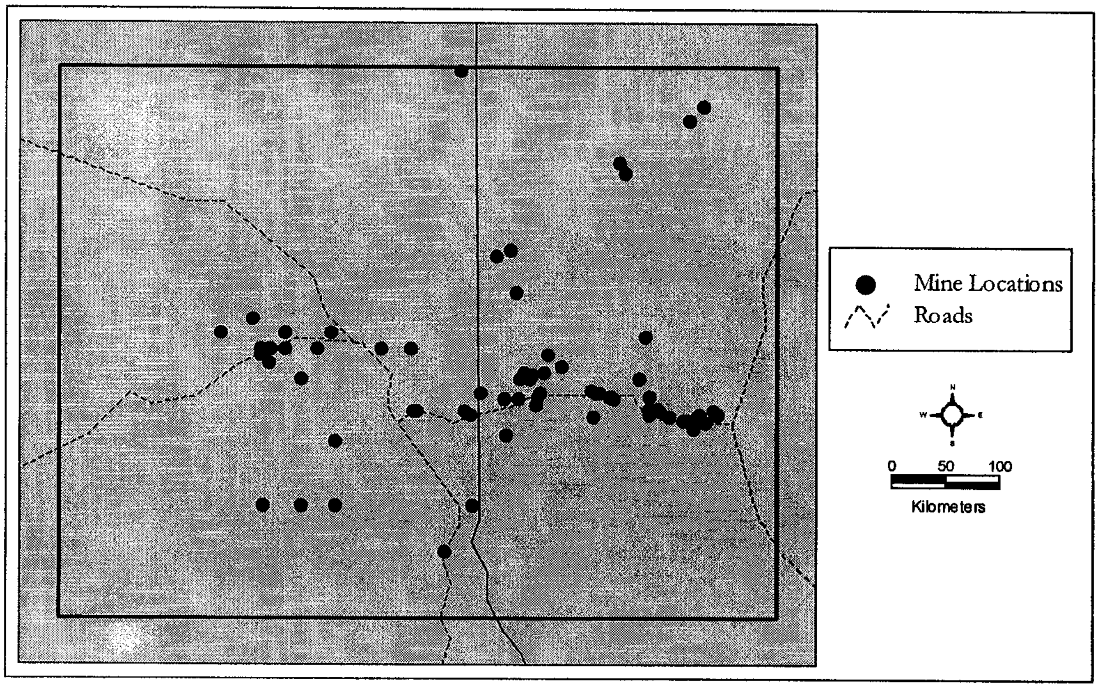


For southern Ontario (ON) dabblers there was no significant difference in $Pb^{206:207}$ signatures of elevated vs. non-elevated birds, indicating that the source of Pb exposure may be the same between the two groups, or that the anthropogenic Pb source has a similar isotopic ratio to that of the Pb found in the non-elevated birds. The isotope ratios for these two groups was unlike that for Pb from gasoline combustion in Canada, indicating that the ingestion of soils, sediments, vegetation or other biota contaminated with Pb from gasoline combustion is not a prominent source of exposure in southern Ontario dabblers. The mean $Pb^{206:207}$ signatures of 1.19 closely match that for Pb shot pellets and non-precambrian Pb ores. However, taking into consideration that mining is not a prominent activity in the highly populated southern Ontario study block and the significant decrease in bone Pb concentrations and proportion of birds with elevated levels of Pb, I feel that the source of Pb exposure in these southern Ontario dabblers is most probably due to Pb shot ingestion. This exposure may be result of either: 'old' Pb pellets remaining from years of Pb shot use prior to the ban or from 'new' Pb deposited by hunters failing to comply with the ban. Since ingestion of Pb shot by waterfowl and subsequently elevated levels of bone Pb, is partially dependent upon the amount of Pb shot available, it is likely that these birds were exposed to 'old' Pb. This is in agreement with Anderson et al. (2000) who concluded that the 31.8% of ingested Pb in Mallards from the Mississippi Flyway was due to Pb shot deposited prior to Pb shot restrictions. Recent Trumpeter swan die-offs due to lead poisoning in BC and Washington state have been most likely a result of ingestion of 'old' shot (WDFW, pers. com).

Dabblers from the Rouyn-Noranda study block also did not have significantly different $Pb^{206:207}$ signatures between elevated and non-elevated birds, suggesting a common origin of Pb exposure. The main source of lead exposure in this area is currently unclear. The mean $Pb^{206:207}$ signature of 1.15 does not closely match the mean $Pb^{206:207}$ signature for Pb shot (1.19), yet it is similar to the $Pb^{206:207}$ signature of the most popular lead shot used in Quebec (Challenger-1.16; see Table 3.1). In addition, the dramatic decline in bone Pb concentrations suggests that, at least previously, lead shot was a major source of elevated lead levels in waterfowl of this area.

The Rouyn- Noranda study block has a high density of mining and smelting activities (Figure 3:16) with the Horne smelter in Noranda a prominent feature, however Pb ore deposits mined in the Noranda area typically have low isotopic ratios. For example, Franklin et al. (1983) reported the Noranda Galena $Pb^{206:207}$ signature to be 0.92, which is in agreement with Sturges and Barrie (1989) who reported a composite of Noranda smelter dust, analyzed for an Environment Canada inter-laboratory comparison to have a $Pb^{206:207}$ signature of 0.996. However, the Horne smelter is a custom copper smelter and uses feedstock Pb ores from a variety of sources with varying Pb isotope compositions, most containing higher ratios, (e.g. Europe isotopes 1.10-1.15) (Hou et al. unpubl. data), which would result in intermediate isotopic ratios. This is in agreement with Sturges and Barrie (1989) who measured $Pb^{206:207}$ signatures in aerosol samples from a rural location in central Ontario (Dorset) in 1983-84 and concluded that the emissions from the Northern Quebec industrial source can be characterized by an isotope ratio equal to the lowest $Pb^{206:207}$ signature recorded at Dorset (1.01). Intermediate ratios (1.06-1.13 with a mean of 1.12) were considered to be a result of mixing with Canadian vehicular Pb as well as from recycling of Pb with varying isotopic compositions. Thus, the current primary source of Pb exposure in dabblers from the Rouyn-Noranda study block may be a result of the ingestion of soils, sediments or vegetation contaminated from a combination of Pb particles deposited into the environment from past combustion of leaded gasoline and the smelting of Pb ores and the ingestion of Pb shot pellets, or soils contaminated with the Pb particles from pellets.

Figure 3.16 Mine locations in the Rouyn-Noranda study block



3.3.2 American Woodcocks

Young of the year (YY) American woodcocks have shown, overall, a slight yet significant increase in bone Pb concentrations (21.21 μg/g vs. 18.69 μg/g) since 1995. In agreement with Scheuhammer et al. (1999), I observed a west to east increase in average bone-Pb levels as well as in the proportion of birds with elevated levels of Pb (>20 μg/g). The observed regional differences in mean bone-Pb concentrations and in the proportion of birds with elevated Pb are not readily explainable. Scanlon et al. (1979) reported Pb levels in the feathers of 1, 008 woodcock from 32 states of the U.S to be 12.9 μg/g (dw). While there were geographic differences noted among the states, no pattern was evident and samples collected from Maine, which borders New Brunswick and Nova Scotia, showed lower than average feather-Pb concentrations (<10 μg/g). This is relatively high in comparison to other birds. For instance, 93% of the Wild turkeys measured in remote and presumably uncontaminated areas of Virginia, had lead levels in feathers <10 μg/g (Scanlon et al. 1978). In a review, Burger (1993) reported that only 6% of the studies measuring feather-Pb concentrations in wild birds exceeded mean concentrations greater than 10 μg/g.

The magnitude of Pb exposure and subsequent mortality from Pb poisoning in non-waterfowl species have not been well studied. However, given the significant incidence of elevated bone Pb concentrations in YY woodcocks in eastern Canada, identification of the source of exposure is important. Potential sources of exposure in woodcocks include the ingestion of Pb shot pellets deposited into the environment by hunters. The exposure to Pb shot is greatest when three conditions are met: high shot density, environmental conditions that result in the shot being available to birds, and feeding habits that result in shot ingestion. Most of the research on Pb poisoning in birds has focused on waterfowl and their predators rather than upland game, however in their review, Locke and Friend (1992) reported Pb poisoning due to ingestion of Pb shot in 31 species other than waterfowl. While it has not been documented that American woodcocks ingest Pb shot, reports of Pb ingestion have been documented within the family Scolopacidae. For example, Hall and Fisher (1985) observed that feeding behavior and bill length increased the risk of shot ingestion. They reported that marsh birds, such as the Long-billed dowitcher (*Limnodromus scolopaceus*) and Marbled gowit (*Limosa fedoa*), which, like woodcocks, typically probe sediments for food and grit, were at particularly high risk for shot ingestion. In Canada, Kaiser et al. (1980) reported 1-5 ingested Pb shot pellets in 9% of 54 Dunlins (*Calidris alpina*) collected after they had collided with power transmission wires.

Various species of birds (e.g. Ring–necked pheasants, Bobwhite quail and Mourning doves) are known to ingest Pb pellets from agricultural fields (Sanderson and Bellrose 1986), which woodcocks also frequent for roosting, courtship displays and foraging. (Keppie and Whiting 1994). Density of Pb shot on the surface of cultivated fields varies with the time of year or the proximity to hunting season (Kendall et al. 1996). For example, in Tennessee, Lewis and Legler (1968) reported a post-hunting shot density of 107,637 shot/ha in the top 0.95 cm of soil on a dove field that had 8 years of heavy use by hunters. Semel et al. (1987) reported higher levels of spent shot (333,674 shot/ha) along fencerows adjacent to a cultivated field at a shooting preserve in Illinois, rather than in the field itself (79,312 shot/ha). Castrale (1989) demonstrated that shot densities in untouched fields increase rapidly after one hunting season. In 13 fields in Indiana, shot densities increased 645% in the top 1.3 cm of soil, after a single season of dove hunting. Normal tillage practices in 6 of these fields reduced shot densities by an average of 73%. Peters and Afton (1993) examined the effects of deep tillage on the redistribution of artificially seeded Pb shot at Catahoula Lake, Louisiana. All deep tillage techniques resulted in redistribution of shot from the top 10 cm of soil to lower strata as compared to controls. In control sites, 92% of Pb shot was recovered above 10cm, while for deep tilled sites, >86% of the pellets were recovered below 10 cm.

Ingestion of Pb pellets is not the only way for woodcocks to be exposed to this form of Pb. Pellets deposited into the environment slowly oxidize and the Pb becomes bio-available in the soil (Jorgensen and Willems 1987). Thus, the ingestion of contaminated soil and/or food may be another important source of Pb exposure for American woodcocks. The woodcock's main food items (82% earthworms and other invertebrates) (Keppie and Whiting 1994) are coated with soil and likely contain ingested soil in their digestion tract. In particular, earthworms, which often comprise as much as 90% (dw and volume) of the woodcocks diet, can accumulate concentrations of Pb from contaminated soils (Beyer et al. 1982), and subsequently pass on this Pb to the woodcock.

In addition, like waterfowl, woodcocks are also susceptible to Pb deposited onto the soil, water and vegetation from industrial activities such as past combustion of leaded gasoline and non-ferrous mining and smelting activities.

A comparison between YY woodcocks with elevated and non-elevated levels of bone Pb showed a significant difference in $Pb^{206:207}$ signatures. Consistent with Scheuhammer et al. (1999), neither elevated or non-elevated ratios were similar to those for leaded gasoline or Canadian Precambrian Pb ores, but rather match more closely with the mean ratio for Pb shot pellets. The increase in bone Pb concentrations and an isotopic ratio similar to Pb shot is consistent with the fact that woodcocks are still legally hunted with Pb shot pellets, thus this source of Pb continues to be deposited into their environment and is subsequently available through ingestion of the pellets themselves or through the ingestion of Pb contaminated soil/food.

Chapter 4 Determination of Hunter Compliance with the 1999 National Ban on the Use of Lead Shot for Hunting Waterfowl

4.1 Introduction

It has been accepted and documented that the ingestion of Pb shot pellets was the primary source of Pb exposure in waterfowl prior to regulations against the use of Pb shot for hunting waterfowl (Sanderson and Bellrose 1986; Scheuhammer and Templeton 1998). For the conservation of waterfowl, their avian predators (e.g. Bald eagles, Red-tailed hawks and Great horned owls) and for the health of the environment, restrictions on the use of Pb shot have been implemented in both Canada and the U.S.

The earliest non-toxic shot requirements in the US began in 1976 with the implementation of non-toxic shot zones in areas where 5% or greater of the waterfowl population sampled had more then one Pb pellet in the gizzard or tissue levels above allowable background levels. The phase-in of a nationwide ban on the use of Pb shot for hunting waterfowl began in the 1987-88 hunting season and was in full effect for the 1991-1992 hunting season. (USFWS 1999). Restrictions on the use of Pb shot for upland game are currently left to state agencies and vary in the level of restriction. Currently, 23 states have implemented some sort of upland game non-toxic shot regulations. All states have indicated that these regulations were implemented to reduce potential ingestion of lead by waterfowl (WDFW 2001). Nationwide, 1.33 million acres of upland game habitat are included in nontoxic regulations, 60% of which is found in two states: Nebraska and South Dakota.

In Canada, restrictions began in 1991 with the implementation of similar 'non-toxic shot zones.' These zones were demarcated based upon areas where Pb poisoning problems had been documented; where elevated (>80 μg/100ml) blood Pb levels in dabblers exceeded 5%; or where shot ingestion rates in dabbling ducks exceeded 10% (Wendt and Kennedy 1992). In September 1997, restrictions on the use of Pb shot increased to include all areas within 200 meters of any watercourse. Finally, in September 1999, a nationwide ban on the use of Pb shot for hunting migratory game birds, except for American woodcocks, Band-tailed pigeons (*Columba fasciata*), and Mourning dove went into effect. The intent of these restrictions was to reduce the availability of Pb shot to high-risk migratory birds. However, decades of hunting have resulted in high densities of Pb shot remaining in some areas (Sanderson and Bellrose 1986), which may still be available to waterfowl.

Currently Pb shot is still used for hunting upland game birds (e.g. American woodcocks and Mourning doves) and small mammals (e.g. rabbits and squirrels), as well as for clay target shooting in the U.S. and Canada. The amount of Pb deposited into the Canadian environment from these sources has been estimated at approximately 66% (1,400 tons/year) of the Pb deposited prior to restrictions on Pb for hunting waterfowl (Scheuhammer and Norris 1995). Despite regulations banning Pb shot for hunting waterfowl, Pb poisoning remains an important cause of mortality for migratory birds and their predators. For example, 159 trumpeter swans died due to Pb poisoning in the winter of 2000-2001 and an additional 138 died in the winter of 2001-2002 in Western Washington according to wildlife biologists of the Washington Department of Fish and Wildlife (WDFW)(Mike Davidson, pers. Com.). While the source of Pb exposure has been attributed to the ingestion of Pb shot pellets found in the gizzards of many of the dead birds, the origin of these pellets remains a mystery.

In bald and golden eagles, the major source of Pb exposure and Pb poisoning is believed to be from ingestion of Pb shot and Pb bullet fragments ingested by or embedded in tissues of prey, particularly waterfowl, upland game birds and small mammals (Kendell et al. 1996, Scheuhammer and Norris 1995). Between 1990-1996 Wayland and Bollinger (1999) found that 12% of 127 bald and golden eagles found dead in the prairie provinces of Canada were Pb-poisoned and an additional 4% were sub-lethally exposed. For Bald eagles (*Haliaeetus leucocephalus*), Pb shot imbedded in waterfowl appeared to be the primary source of Pb shot pellets or fragments, while for Golden eagles (*Aquila* *chrysaetos*), a species that feeds exclusively on terrestrial upland prey, small mammals and upland game birds were more likely the source of Pb exposure. Platt (1976) investigated the diets of Bald eagles wintering in the high deserts of western Utah. Their diets consisted of mainly terrestrial animals with 98% of the >115 pellets collected containing rabbit fur. In addition, Pb shot (usually size No. 4, the most popular load for rabbit hunters) was found in 71% of these pellets.

Meretsky et al. (2000) reported 6 cases from 1997 and 1998 of Pb poisoning (the birds were recaptured and treated with chelation therapy) and 7 cases of low-level Pb exposure in released California condors (*Gymnogyps californianus*). This study reported Pb poisoning of California condors to be the primary cause of mortality, both historically and for the future. This prediction was validated when five California condors released in northern Arizona died in the spring and summer of 2000 from Pb poisoning and two other condors underwent chelation treatment for Pb toxicity. In one condor, 17 Pb shot pellets were found in the digestive system and liver Pb level was 34 μg/g (wet wt) (S. Farry, pers. comm.)

Although a large-scale survey to determine the degree of Pb exposure in certain common duck species was conducted in Canada before any restrictions on the use of Pb shot were established (Scheuhammer and Dickson 1996), no studies have been conducted to assess the effectiveness of these regulations. In the preceding chapter, I presented data to show that Pb exposure in 3 species of ducks in Canada has declined substantially since regulations prohibiting the use of Pb shot for waterfowl hunting have come into effect. In this chapter, I describe the results of supplementary studies to estimate the level of hunter compliance with the national Pb shot ban.

4.2 Methods

4.2.1 Regional hunter survey

A total of 4,000 migratory bird permit holders were randomly selected from the national CWS Harvest Survey database (which contains names and addresses of all licensed migratory bird hunters in Canada) for British Columbia and southern Ontario. These two areas were selected because they exhibit relatively high waterfowl hunting activity. Waterfowl bones from the same areas were used in the Pb isotope analyses of the preceding chapter and bone Pb concentrations can thus be used in conjunction with the present hunter survey results to assess the level of compliance among hunters.

The names and addresses of all 4,000 permit holders were carefully screened for duplicate entries and insufficient addresses. Each hunter was then sent an anonymous questionnaire (see Appendix A) with simple questions regarding the use of Pb shot for hunting game birds in Canada.

The main intent of the questionnaire was to estimate the level of compliance with the ban on Pb shot reported by hunters. The first two questions were asked to establish what type (waterfowl or upland game) of hunting each respondent took part in. Because Pb shot is allowed for hunting upland game birds and not waterfowl, this is important information. The third and fourth questions pertained to whether the respondent or anyone they knew used Pb shot for hunting waterfowl, or upland game birds. Question four specifically avoided asking the hunter if they themselves used Pb shot in order to minimize the number of hunters who might either not answer the question or would lie about it since the use of Pb shot for hunting waterfowl is illegal. Questions 5 and 6 were asked due to some suspicions that a portion of hunters might be loading steel shot cartridges with Pb and to help corroborate a cartridge search performed along the Ottawa River (see section 4.2.3). Question 7 was asked in order to provide the hunters a chance to voice their opinions on the non-toxic alternatives available to them. Finally, question 8 was asked in an attempt to more precisely determine the geographic area in which the respondents do most of their hunting.

The questionnaires were sent out in early March 2002. Hunters were given until April 21, 2002 to respond. Responses from returned questionnaires were entered into an electronic database (Microsoft Access 97) for analysis.

4.2.2 Regional law enforcement officer survey

Questionnaires (see Appendix B) asking about the frequency of infractions of using Pb shot given over the past few years were sent via email to regional Federal conservation offices in both BC and Ontario.

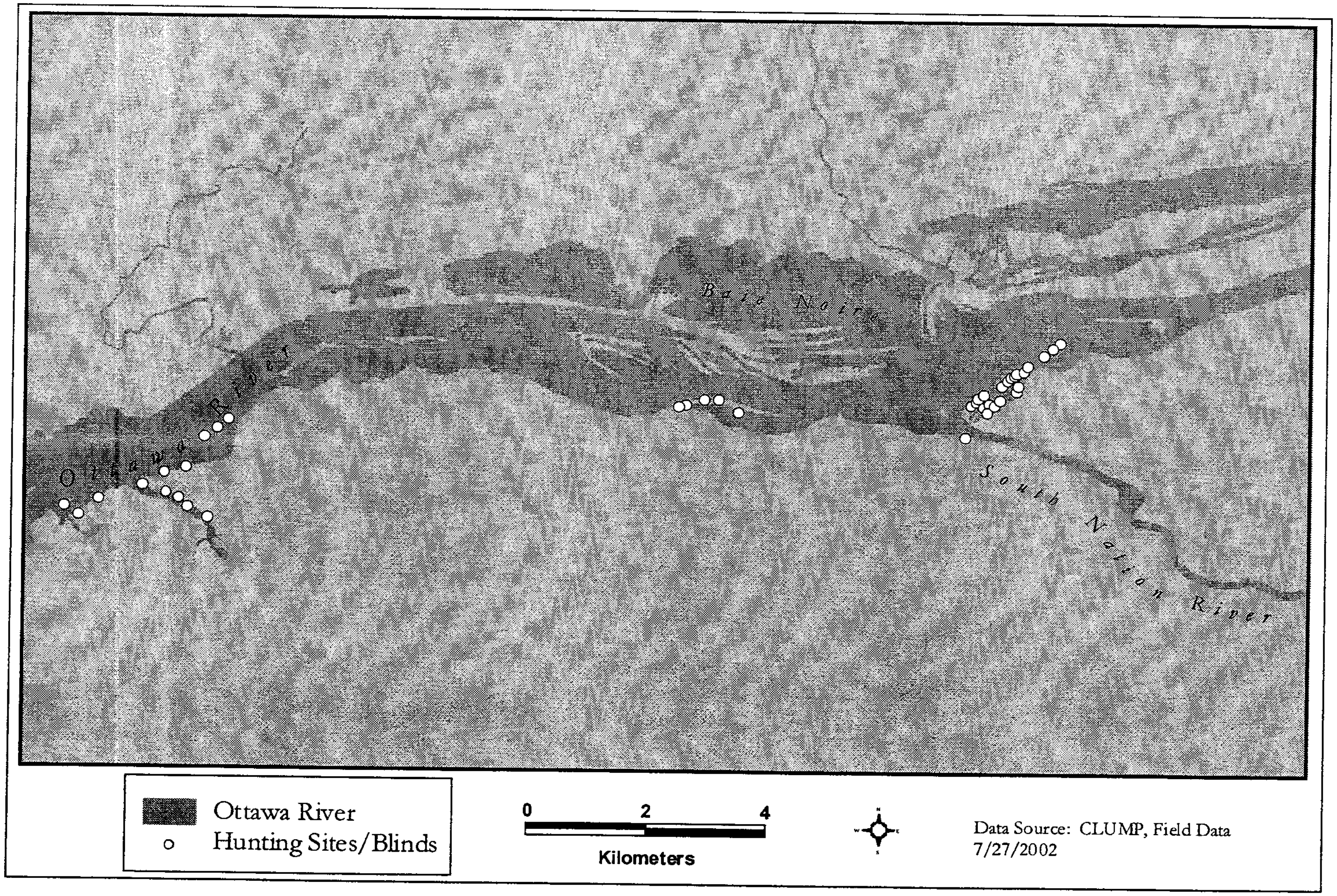
4.2.3 Cartridge Pick-up

On December 9th and 10th 2001, approximately 38 known waterfowl hunting sites/blinds were visited along the Ottawa River, east of Ottawa (see Figure 4.1). The hunting sites/blind locations were provided by a CWS Ontario region enforcement officer. These sites were noted as popular hunting locations along the Ottawa River with some incidences of Pb shot use recorded or suspected by CWS enforcement.

I and two assistants reached most locations by a 14-foot motorized aluminum skiff. Each site was thoroughly searched and spent cartridges left by hunters were collected when found. Dry land blinds were traversed along the shoreline and up to 100 meters inland. Vegetation was shifted and searched for any cartridges. At all water sites (areas where no or little land is present), water and vegetation in and around blinds was scanned for cartridges and aquatic vegetation searched. All hunter-made structures were investigated for empty cartridges.

Collected cartridges were place in plastic bags and the latitude and longitude recorded using a Garmin portable 12-channel GPS.

Figure 4.1 Map of popular duck blinds along Ottawa River, Ontario Canada

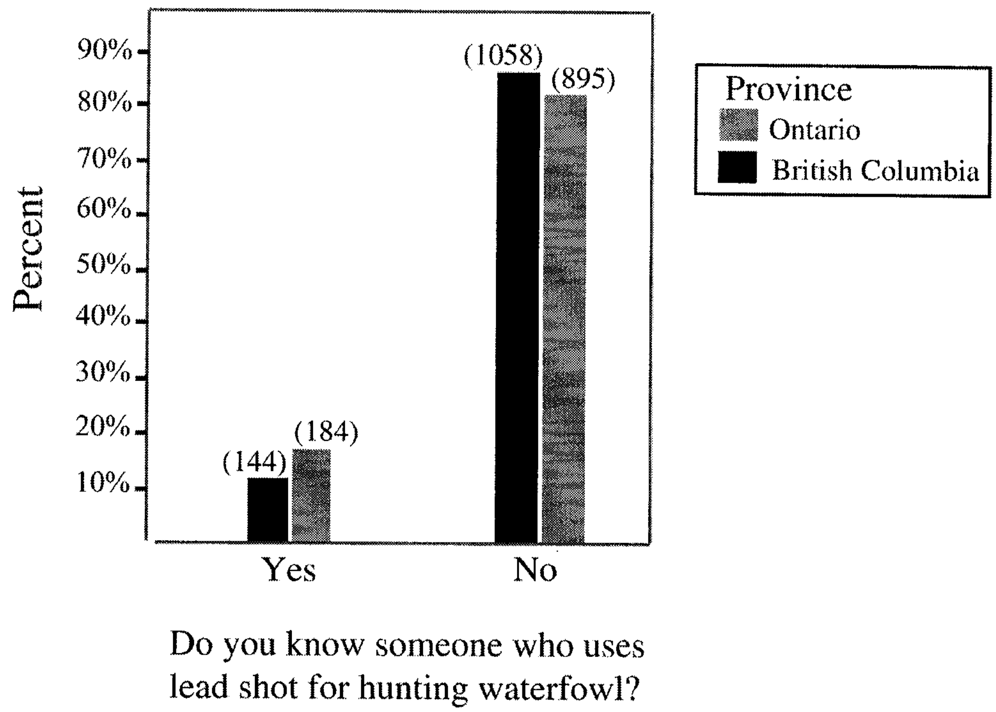


4.3 Results

For the province of British Columbia, 1,953 questionnaires were sent out after an initial screening process had eliminated 47 duplicate entries or insufficient addresses. An additional 42 questionnaires were discarded, as these were undeliverable for various reasons. Sixty-six percent (1,280) of the questionnaires were answered and returned. Of these, 17 questionnaires were discarded because the permit holders answered 'no' to both questions 1 (do you hunt waterfowl) and 2 (do you hunt upland game birds), bringing the total answered questionnaires to 1,221. Of these, 144 hunters (11.8%) answered that they knew someone who used Pb shot for hunting waterfowl (Figure 4.1). A total of 1,024 permit holders reported that they hunted upland game birds, of which 74% used Pb shot.

When asked if hunters found the non-toxic alternatives effective (Figure 4.2), 724 (59.3%) said yes. However, 6% and 1.8% were concerned about the increased injuries to birds with steel shot and the high costs of alternatives, respectively. Hunters in BC are apparently picking up after themselves, with 85.3% (1,041 hunters) reported that they pick up their empty cartridges after hunting.

Figure 4.2 Hunters' response to question about the current use of Pb shot for hunting waterfowl.



For southern Ontario, after the initial screening for duplicates and insufficient addresses, 1,992 questionnaires were sent out to migratory permit holders. Seven questionnaires were returned to sender as undeliverable and were discarded. Twenty hunters either did not answer the questionnaire or answered 'no' to both questions 1 and 2, and these were also discarded. A total of 1,084 (54.4%) answered questionnaires were returned and analyzed. One hundred and eighty four hunters (16.9%) in Ontario reported knowing someone who uses Pb shot to hunt waterfowl (Figure 4.1). Nine hundred and ten permit holders in southern Ontario reported that they hunt upland game birds of which 680 (75%) used Pb shot.

When asked if hunters are satisfied with the available non-toxic alternatives to Pb, 459 hunters (42.1%) responded positively (Figure 4.2). However of the 459 hunters, 4.3% expressed concerned about the injuries to birds steel may be causing and 3.5% felt that alternatives are too expensive. Most (81.1%) Ontario hunters reported that they pick up their empty cartridges.

The proportion of hunters in both provinces (BC and Ontario) who answered 'yes' to questions 3, 4, 5 and 7 are shown in Table 4.1.

Figure 4.2: Hunters' responses to question: "Do you feel that the available non-toxic shot products (steel, and others) are effective for hunting waterfowl?" for British Columbia (BC) and Ontario (ON).

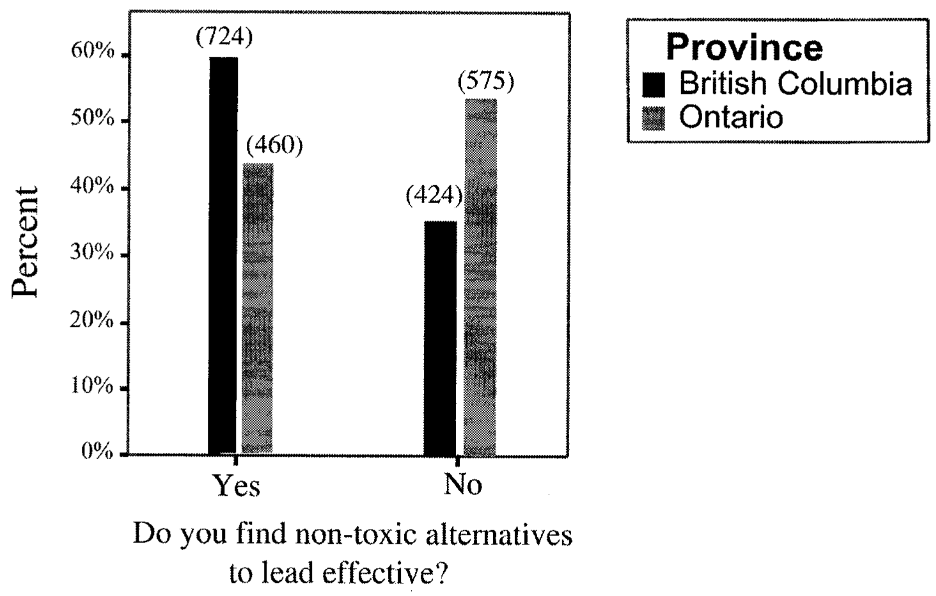


Table 4.1: Proportion of registered permit holders who answered yes to survey questions 3, 4, 5 and 7.

Province	*Rate of Return*	*Uses Pb shot to hunt upland game birds*	*Knows someone who uses Pb shot for hunting waterfowl*	*Picks up empty cartridges*	*Satisfied with non-toxic alternatives*
BC	65.5	74.0	11.8	85.3	59.3
Ontario	54.4	75.2	16.9	81.5	42.1

For the Federal enforcement officer survey, no response came from BC and only a summary of three officers from Ontario was received. The Ontario officers estimated 10-35% of waterfowl hunters checked over the previous two years either had Pb shot ammunition on their person or were charged for still using Pb shot to hunt waterfowl. The majority of these infractions were in rural eastern Ontario. The officers estimated that only about 1% of hunters reload Pb shot into steel shot cartridges.

Along the Ottawa River, spent cartridges were found in six of the 38 blinds visited; a total of 89 cartridges were found. All shells found were for steel shot; no evidence of Pb shot use was found in the area.

4.4 Discussion

Based on the answers provided by migratory bird permit holders in British Columbia and southern Ontario, compliance with the national ban on Pb shot is high (>80%) in these provinces.

However, the estimates of hunter compliance in this survey may be somewhat biased due to the nature of the survey. The fact that the use of Pb shot for hunting waterfowl is illegal may inhibit those hunters who are not complying with the law from taking part in the survey; or those hunters may have lied about using Pb shot. Thus, my survey results may be an overestimation of the level of compliance with non-toxic shot regulations in Canada. On the other hand, the fact that the questionnaire was totally anonymous, plus the impersonal nature of the question regarding Pb use for hunting waterfowl, should have minimized this bias.

The reported compliance levels I observed in the current survey were lower then earlier studies of compliance levels among waterfowl hunters in the U.S. For example, Havera et al. (1994) summarized a number of studies conducted to measure waterfowl hunter compliance in the U.S. between 1976 – 1987. Research techniques varied from hunter surveys, gizzard checks and shot shell collections. Hunter surveys showed a higher compliance rate (~88%) than gizzard checks (~74%) or collection of Pb and steel shot shell wads (~75%).

However, Havera et al. (1994) used a metal detector to differentiate between Pb and steel pellets embedded in hunter-harvested ducks in Illinois. They found that compliance among hunters had increased from 90.8% in 1989 to 98.9% in 1991.

In the 1996-97 hunting season Anderson et al. (2000) examined 16,651 gizzards from ducks harvested along the Mississippi Flyway. Mallard ingestion rates (8.9%) of pellets were similar to previous data (8.4%-Bellrose 1959; 7.8%-Anderson et al. 1987), however Mallards in the upper and middle regions of the flyway had higher proportions of nontoxic pellets in their gizzards than did the Mallards from the lower region. Approximately 68% of the Mallard gizzards with ingested shot contained only non-toxic shot and 8.9% contained both toxic and non-toxic shot. Ingestion rates among diving ducks (Ring-necked and scaup), were found to be lower then previously reported. However, unlike Mallards, 53% of the pellets ingested were Pb, indicating that in the 1996-97 hunting season Pb pellets were more readily available to diving ducks than to dabblers. For diving ducks that had ingested pellets, 45.3% of the Ring-necked ducks, 44% of the scaup and almost 71% of the Canvasbacks contained only non-toxic shot. Anderson et al. (2000) also found that of the 1,318 gizzards positive for imbedded (rather then ingested) pellets: 98.9% of the Mallards, 97.8% of the Ring-necked ducks, and 100% of the scaup and Canvasback gizzards, contained only non-toxic pellets. This high level of nontoxic shot found in all species examined throughout the Mississippi Flyway indicate a high level of compliance among hunters with the ban on Pb shot and corroborates the findings of Moore et al. (1998) who concluded that Pb shot pellets ingested by birds are likely from 'old' Pb shot deposited prior to the ban.

Moore et al. (1998) found ingestion rates in the 1992-93 hunting season among Canvasbacks and Lesser scaup in Louisiana to be similar to pre-ban (1988-89) rates, but with a significant reduction in the prevalence of ingested Pb shot. Samuel and Bowers (2000) documented a 44% decrease in blood Pb levels of American black ducks in Tennessee since 1986-88.

Among hunters, the objections against restrictions on the use of Pb shot for hunting waterfowl were that 1) the primary nontoxic alternative (steel) is ballistically inferior to Pb and probably causes increase crippling of waterfowl; and 2) non-toxic alternatives tend to be more expensive than Pb. Interestingly, these objections are still prevalent today, even after many years of Pb shot restrictions. In my survey, it is apparent that hunters are complying with the regulations, but they are unhappy about it. More than 50% of the hunters in Ontario and 40% of the hunters in BC were of the opinion that non-toxic alternatives were not effective for waterfowl hunting. This perception is perhaps a result of poor communication and education efforts between governmental wildlife management agencies and hunters. The strongly held belief that steel "cripples more birds" due to its perceived inferior ballistics may also be a factor in the decline in the sale of annual hunter permits.

Crippling loss, the un-retrieved killed or injured bird, occurs in all hunting and has been a serious issue prior to the use of steel shot. Bellrose (1953) reported that 22.5% of the birds knocked down (using Pb shot) were not retrieved. The U.S Fish and Wildlife Service estimated that the national average for annual crippling loss rate for all waterfowl was 20% at a time when non-toxic alternatives to Pb were virtually non-existent (Anderson and Burnham, 1976). Using this criterion, Norton and Thomas (1994) estimated that 1.6 million ducks were lost to crippling in 1992 in prairie Canada and the US combined. The majority of crippled birds do not survive as Van Dyke (1981) documented in 1977 and 1978. He found the recovery rate of crippled mallards on a national wildlife refuge in Wisconsin to be less then 3% and noted that weight loss contributed either directly or indirectly to the deaths of most of these crippled birds. Therefore, the concern about crippling is warranted, however it has not been clearly demonstrated that the proper use of steel shot results in increased crippling rates. For example, Andrews and Longcore (1969) compared a commercially available No. 4 Pb shot to an experimental No. 4 steel shot at the U.S. Fish and Wildlife Service Patuxent Wildlife Research Center. They detected no difference in crippling rates or performance (bag rate) between the two shot types at distances of 30 –65 meters. Nicklaus (1976) investigated the effects of Pb and steel shot on pen-reared mallards harvested from a shooting preserve in Illinois. He also found no significant differences between the number of ducks crippled by Pb or steel shot. Mikula et al. (1977) conducted a field test of steel and Pb shot in Michigan. Up to approximately 32 meters; the crippling loss for steel (16%) was slightly higher than for Pb (13.6%), but this difference was not found to be statistically significant. Consistent with the above findings, Humberg et al. (1982) also found no differences in the bagging or crippling rates between Pb and steel shot.

In contrast, Cochrane (1976) found that the overall performance of No. 4 Pb shot was superior to No. 4 steel shot. The Pb shot bagged more and crippled fewer ducks than steel shot. However, steel shot crippled fewer birds at further distances than did Pb shot. Maximum crippling loss for No. 4 steel and No. 4 Pb shot occurred at 60 and 70 meters, respectively. Hebert et al. (1984) reported that the use of No. 4 steel shot resulted in a 42% increase in crippling rate over No. 6 Pb shot.

Due to the diversity of test conditions and parameters, the studies discussed above attempting to determine the efficiencies of Pb and steel shot for harvesting waterfowl, have produced results that are inconsistent and not comparable (USFWS 1986). However, with improved technology and a better understanding of the ballistic characteristics of steel, many of the problems associated with steel have been eliminated.

It is believed that hunter technique and skill rather then shot type is the main source of crippling in waterfowl. The ballistic properties of steel and Pb differ. Steel shot is lighter, produces denser patterning, shorter shot strings and a lower retained velocity (or knock down power) at longer ranges then Pb. With these properties in mind, one cannot hunt effectively using the same techniques for steel as for Pb. For example, for steel pellets to approximate the velocity and penetration of Pb, one must use a larger (heavier) steel pellet. It is recommended that with steel pellets, at least two shot sizes larger than Pb be used (Brister 1992; Scheuhammer and Norris 1995). Herbert et al. (1984) documented that hunters using 'Pb shot techniques' with steel pellets had 42% higher crippling rates compared to hunters using Pb pellets and 'Pb shot techniques'. Nieman et al. (1987) estimated hunter performance and crippling loss in Prairie Canada (Alberta, Manitoba and Saskatchewan). The number of birds crippled varied with hunting method (i.e. pass shooting and sky-busting) resulted in more crippled birds than did decoy shooting. Hunting over water also resulted in more crippling loss than did field hunting as hunters were often not equipped to retrieve birds.

Cochrane (1976) found that embedded shot and broken bones were both correlated with shooting distance and with each other. The number of broken bones and embedded shot decreased with distance, indicating that the number of pellets and the distance at which a duck is shot determines the probability that a duck will either be bagged or crippled. Anderson and Sanderson (1979) documented that crippling of Canada geese increased with range for both Pb and steel. Nicklaus (1976) noted that the crippling rate was in part reflected by the ability of the hunters to find downed birds, which in turn varied with the type and condition of vegetation at the hunting site.

The undesirable effects of hunting with steel shot are restricted to crippling losses. However, the detrimental effects of Pb shot usage are far greater and include crippling losses, losses from lethal and sub-lethal Pb poisoning of waterfowl and their predators, unnecessary Pb exposure for humans consuming game bagged with Pb shot, and the breakdown of Pb pellets deposited into the environment and subsequent bio-availability of Pb particles to plants and animals (Scheuhammer and Norris 1995).

Currently available non-toxic shot shell loads include: steel, tungsten-based shot (includes tungsten-iron, tungsten-nickel-iron and tungsten polymers), bismuth (a bismuth/tin alloy), and tin. The added cost for hunters purchasing these non-toxic alternatives is difficult to quantify precisely as prices in ammunition vary throughout North American and among the different brands, quality and quantity of the shot, and retail stores. Initial manufacturing and retail costs for steel shot were significantly higher than they are today, however increased public demand due to non-toxic shot regulations has moderated the costs of steel. Current steel shot loads cost approximately $0.25 (USD) per shell, versus about $0.20 per shell for high-quality Pb, and almost $2.00 per shell for equivalent non-toxic loads such as tungsten and bismuth (WDFW 2001). Filion et al. (1993) estimated expenditures incurred by Canadian waterfowl hunters in 1991 to be approximately $450 (CND) per person. Of this, 41.6% was used for equipment purchases, 24.9% for transportation, 12.1% for food, 5.5% for accommodation and 15.9 % for other items. In the U.S., the average yearly expenditure for migratory bird hunters is $470. Of this, 8.5% ($40) is spent on ammunition, while approximately 47% ($222) is spent on trip-related expenditures (lodging, transportation, land use fees, etc) (USFWS 2001). Clearly, ammunition purchases represent a minor part of the average hunter's yearly expenditure.

As shown by the results of the hunter survey, a large majority of the hunters in BC and Ontario appear to be in compliance with the ban on Pb shot, despite cost and concerns about the perceived increase in crippled birds. Results from this survey corroborate my wing-bone study, which demonstrated that Pb exposure in young ducks in Canada has declined substantially since Pb shot regulations were established. Furthermore, the high proportion of hunters still using Pb shot to hunt upland game birds may be the primary source of Pb exposure that contributed to the significant increase in bone Pb levels I observed in YY American woodcocks. Without the ban on lead shot, an estimated 0.5-1.3 million birds in Ontario alone will succumb to lead poisoning. Using the percent decline in elevated bone Pb levels (49%) as a rough estimate for mortality decline, approximately 0.2 to 0.6 million birds will be spared from fatal Pb poisoning. This is a direct result of the high level of compliance among hunters and both waterfowl hunters and conservation officers should be commended for their support of nontoxic shot regulations.

Chapter 5 Conclusion

The purpose of this project was to determine what is currently the most important source of Pb exposure in migratory game birds and to determine if hunters are complying with the 1999 national ban on the use of Pb shot for hunting waterfowl. Bone Pb concentrations in waterfowl have dramatically declined (>58%) since the ban on lead shot for hunting waterfowl went into effect, while bone Pb levels in American woodcocks have significantly increased (12%). The decline in bone Pb levels of waterfowl can partially be attributed to the >80% compliance rate among hunters with the ban on lead shot, while the increase in bone Pb levels of woodcocks may be a factor of the continued legal use of lead shot for the hunting of woodcocks and other upland game birds. Furthermore, the decline in bone-Pb levels indicates that lead shot pellets were in fact a major source of elevated bone Pb levels prior to the ban.

Use of stable lead isotopes to identify sources of lead has been complicated with the global distribution of Pb ores and products and the blending of different leads during smelting. However, in this study, stable lead isotope analysis has confirmed that lead shot pellets, most likely 'old' shot left from pre-ban seasons, continue to be a major source of lead exposure to waterfowl in Southern Ontario. In BC, the current major source of lead exposure appears to be from the ingestion of soils, sediments and food contaminated with lead deposited during the years of burning leaded gasoline in combustion engines. The major source of lead exposure in birds in the Rouyn-Noranda region remains unclear yet sources from mining do not seem to add significantly to elevated Pb levels in waterfowl.

The significant increase in bone Pb levels and isotope data for woodcocks along with a reported 75% lead shot use for hunting of woodcocks indicate that lead shot pellets may be the major source of exposure in these birds, however further research must be done to verify how this occurs.

Hunters are currently complying with the ban on lead shot for hunting waterfowl, but they are unhappy about it. This indicates that governmental wildlife management agencies have been ineffective in properly communicating and educating hunters about the use of non-toxic shot. Further effort should be extended in assisting hunters on the proper technique for hunting with non-toxic shot and be kept up to date on the benefits of their efforts in protecting wildlife.

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Get the lead out! Campaign to focus on non-lead sinkers, Minnesota Office of Environmental Assistance (OEA), http://www.moea.state.mn.us/media/03-26-99-1.cfm

Appendix A

Hunter Survey

PLEASE DO NOT SIGN OR WRITE YOUR NAME ON THE QUESTIONAIRE. THIS IS AN ANONYMOUS SURVEY.

Please circle **YES** or **NO**:

1. Do you hunt waterfowl? YES NO

2. Do you hunt upland game birds (any of the following: pheasant, quail, partridge, grouse, woodcock)? YES NO

3. Do you use lead shot to hunt upland game birds? YES NO

4. Do you know anyone who uses lead shot to hunt waterfowl? YES NO

5. Do you pick up your shells when you are finished hunting for the day? YES NO

6. Do you load or reload your own shells? YES NO

7. Do you feel that the available non-toxic shot products (steel, and others) are effective for hunting waterfowl? YES NO

8. Please write below the name of the closest town or city to the area where you hunt waterfowl most often.

____

PLEASE FOLD YOUR COMPLETED QUESTIONNAIRE, PLACE IT IN THE POSTAGE-PAID RETURN ENVELOPE PROVIDED, AND MAIL IT BACK TO ME BEFORE APRIL 21, 2002.

THANKS VERY MUCH FOR YOUR HELP!

Appendix B

SURVEY OF MIGRATORY BIRDS ENFORCEMENT OFFICERS

1. Over the past 2 hunting seasons, what is the approximate percentage of waterfowl hunters that you've encountered who still use, or have in their possession, lead shot ammunition?

2. Over the past 2 hunting seasons, what is the approximate percentage of waterfowl hunters that you've encountered who have reloaded lead shot into a steel shot cartridge?

3. If you've noticed that violations of the lead shot regulation tend to occur in particular locations, please write (on the line below) the general locations where violations tend to occur most frequently. (If this line is left blank, I will assume that the violations you've encountered are spread more or less evenly throughout the hunted areas in your territory).

4. OPTIONAL - In the space below, please provide any other comments you may have regarding your experience with waterfowl hunters and the use of lead shot for waterfowl hunting since the ban on lead shot: